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TECHNO-ECONOMIC ASSESSMENT OF THE REMOVAL OF BENZENE IMPURITIES

Master's thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 8 July, 2016.

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Abstract

In Borealis' aromatics production site benzene is produced as well as imported for further processing to cumene by catalytic alkylation. Objective of this thesis is to find more feasible way to process benzene at Borealis' benzene unit. Three factors are aspired: possibility to source benzene with higher toluene content, avoid distilling on-spec benzene, and allow alkylation catalyst run length match turnaround interval of five years. Three processing scenarios are compared in this thesis: I) distillation of all used benzene, II) distillation of only imported benzene, and III) bypassing the benzene distillation column completely.

Techno-economic assessment of these three scenarios is conducted. Capacity of the benzene distillation column is studied by Aspen Plus simulation. Clay treating as benzene purification method is studied by laboratory tests. Investment needs as well as operating costs are determined for all the scenarios. Net present value (NPV), internal rate of return, and payback time are calculated for the scenarios. Also sensitivity analysis is done for the scenarios and some risks and other factors are compared.

Simulations show that capacity of the distillation column is enough for maximum feed in scenario I. However, some changes to the reboiler of the column must be done so that minimum capacity of scenario II can feasibly be met. In laboratory, three different acid activated bentonite clays are tested for N-formylmorpholine removal by adsorption capability and capacity tests. Operating costs are estimated with steam, catalyst and clay costs. Benefit gained from price difference of benzene with higher toluene content is also taken into account. NPV of the scenario II is calculated to be the best. NPVs are most sensitive for steam price change and change in benzene price difference.

Other factors imply also that the scenario II would be the best alternative. In this scenario, there is a possibility to purchase lower quality benzene, no benzene that is on specifications is unnecessarily distilled over, and the catalyst run length should match the turnaround period with efficient operation of the clay treaters. According to these factors and financial indicators, the scenario II is recommended as processing method of benzene.

Keywords Benzene purification, clay treating, techno-economic assessment

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Tiivistelmä

Borealiksen aromaattien tuotantolaitoksella bentseeniä tuotetaan sekä tuodaan. Bentseenistä valmistetaan kumeenia katalyyttisella alkyloinnilla. Tämän työn tarkoituksena on etsiä kannattavampi menetelmä prosessoida bentseeniä Borealiksen bentseeniyksikössä. Kolmea tekijää tavoitellaan: mahdollisuutta ostaa korkeamman tolueenipitoisuuden bentseeniä, spesifikaatiot täyttävän bentseenin tislauksen välttämistä, ja alkylointikatalyytin toiminnan säilyttämistä viiden vuoden seisokkivälin. Työssä vertaillaan kolmea prosessointiskenaariota: I) kaiken käytetyn bentseenin tislaus, II) vain tuontibentseenin tislaus, III) bentseenin tislauskolonnin ohitus kokonaan.

Näille vaihtoehdoille tehdään teknis-taloudellinen arvio. Bentseenin tislauskolonnin kapasiteettia tutkitaan simuloimalla Aspen Plus -ohjelmalla. Bentseenin puhdistusta savikäsittelyllä tutkitaan laboratoriokokeilla. Kaikille kolmelle skenaarioille kartoitetaan investointitarpeet sekä määritetään käyttökustannukset. Skenaarioille lasketaan nettonykyarvo, sisäinen korkokanta sekä takaisinmaksuaika. Skenaarioille tehdään myös herkkyysanalyysi ja joitakin riskejä sekä muita tekijöitä vertaillaan.

Simulointien perusteella tislauskolonnin kapasiteetti riittää skenaario I:n maksimisyöttömäärälle. Jotta skenaarion II minimisyöttö voidaan toteuttaa, kolonnin pohjan kiehuttimeen on kuitenkin tehtävä muutoksia. Laboratoriokokeissa testataan kolmea happoaktivoitua bentoniittisavea N-formyylimorfoliinin poistamisessa adsorptiokyky- sekä kapasiteettikokeilla. Käyttökustannukset arvioidaan höyrylle sekä katalyytti- ja savikustannuksille. Tolueenipitoisella bentseenillä saavutettava kustannushyöty huomioidaan myös. Skenaarion II nettonykyarvo on paras. Nettonykyarvot ovat kaikkein herkimpiä höyryn hintavaihtelulle ja bentseenin hintaeron vaihtelulle.

Muidenkin tekijöiden perusteella skenaario II on paras vaihtoehto. Tässä skenaariossa on mahdollisuus ostaa alemman laadun bentseeniä, spesifikaatiot täyttävää bentseeniä ei tislata turhaan ja katalyytin käyttöiän pitäisi kestää huoltoseisokkivälin tehokkaan savitornien operoinnin avulla. Näiden tekijöiden sekä talouslaskelmien perusteella skenaariota II suositellaan bentseenin operoinnille.

Avainsanat Bentseenin puhdistus, savikäsittely, teknis-taloudellinen arvio

Preface

This thesis was done for phenol and aromatics production unit of Borealis Polymers Oy during spring 2016. I thank for the opportunity to write my thesis at Borealis of such an interesting subject.

Most of all I want to thank my instructor Tuomas Ouni from Borealis for all the support, guidance and countless advices he provided me during the thesis writing. He always had time to answer my questions and I could not have hoped more from an instructor. I also thank Sarwar Golam, my instructor from Aalto University, for his comments and perspectives for the thesis. Likewise, I want to thank professor Pekka Oinas for his valuable comments and proposals, which improved this work. I also want to thank all the staff from Borealis who helped me during this spring. Especially I want to acknowledge Mikko Lindtman, Santtu Hietala, Markku Wörlin, Kim Tarpila, Gustav Lund and Mikko Rönkä for their time and advices.

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Porvoo, 8.7.2016

Kirsi Linnavuori

Table of Contents

Appendices

Appendix 1: Results of the clay tests

Appendix 2: Instructions for clay tests in laboratory

Appendix 3: CAPEX and OPEX of the scenarios

Appendix 4: Financial indicators of the scenarios

Appendix 5: Sensitivity analysis

Abbreviations

BTX	benzene, toluene and xylene
CAPEX	capital expenditure
EPCM	engineering, procurement and construction management
FCC	fluid catalytic cracking
GC	gas chromatography
IRR	internal rate of return
LPG	liquid petroleum gas
MCH	methylcyclohexane
NPV	net present value
NFM	N-formylmorpholine
NMP	1-methyl-2-pyrrolidone
OPEX	operating expenses
PIPB	polyisopropylbenzene
PBP	payback period
WHSV	weight hourly space velocity

1 Introduction

Benzene is one of the several basic elements in the petrochemicals industry. It is a single-ring aromatic compound, C_6H_6. Benzene is mostly used as an intermediate in the manufacture of industrial chemicals. The main derivatives of benzene are styrene, cumene, and cyclohexane. (Folkins 2000) Cumene is produced from benzene by alkylation with propylene over a catalyst. During recent decades, manufacturing of cumene by benzene alkylation has shifted more and more from old technologies based on solid phosphoric acid and aluminum chloride to zeolite catalyst based liquid phase processes. (Hwang and Chen 2010)

Benzene can be produced from several sources such as oil refining, olefin plants or even steel mills. The two main raw materials of benzene are coal and petroleum. Petroleum has become the main source of benzene as the methods to produce aromatic compounds have improved. (Folkins 2000) Crude oil contains only small amount of benzene, typically less than 1 %. However, more sophisticated processing of crude oil has increased the yield of benzene from petroleum during recent decades. One of the foremost sources of benzene is olefin plants. Benzene is one of the by-products when cracking naphtha or gas oil. (Burdick and Laffler 2010) Depending on manufacturing method, there are always some typical impurities in benzene. When used as feedstock in cumene process the quality standards for benzene are extremely strict. This is because of poisoning and deactivation tendency of the zeolite catalyst due to impurities in reagents.

Borealis Polymers Oy produces benzene from pyrolysis gasoline and reformate at Kilpilahti aromatics plant. The plant is located next to Neste refinery site, and Borealis' petrochemical production units are highly integrated with Neste refinery. Pyrolysis gasoline to benzene unit comes from Borealis' own olefin plants and is processed to benzene. All of the manufactured benzene is processed into cumene, and further into phenol and acetone. In addition to own production, benzene is also imported to meet cumene unit demand. There are several benzene-related challenges

in cumene production. One of the most substantial concerns is quality and purity of produced and imported benzene, mainly because of the sensitivity of the catalyst used in cumene manufacturing.

1.1 Aims of the thesis

At the moment in Borealis' aromatics plant all produced benzene is distilled over to remove toluene and other heavy components. However, the purity of the produced benzene before the distillation is in accordance with specification, apart from some momentary disturbances in the process. Most of the time, the distillation column could be bypassed. Distillation of all produced benzene requires a lot of energy and causes expenses, so there is a great interest to replace the distillation with some other processing method or to bypass the column. Risks of impurities of benzene in the next process step, in the cumene unit, are however so high that the distillation cannot be bypassed without any precaution or alternative purification method. Imported benzene is fed to the cumene unit mixed with the self-produced benzene. All benzene fed to the cumene unit is treated with clay to remove some impurities. Clay purification is based on adsorption. Possibility of different contaminants in imported benzene causes challenges. These impurities are harmful to the cumene catalyst, and there has been discussion of distillation of imported benzene to remove them. This would also give an opportunity to purchase cheaper benzene with higher toluene content.

In this thesis the main goal is to find a technologically and economically feasible method to bypass the benzene distillation column or to find more suitable method to operate benzene purification process without risking the quality of benzene. The aim is to avoid distilling benzene that is on specifications and to allow cumene catalyst operating length match plant's turnaround interval. A goal is also to find a way to utilize benzene with higher toluene content. The research question of the thesis is: how can the quality of benzene be techno-economically assured without the final distillation of self-produced benzene?

1.2 Structure and scope of the thesis

The main processes of benzene production in petroleum industry are introduced in chapter two of literature part. These processes are catalytic reforming, hydrodealkylation, disproportionation, and transalkylation of toluene, and steam cracking. These other manufacturing methods are in the scope of the thesis because of the significant amount of benzene imported to the Borealis' aromatics plant. Different separation and purification methods of benzene are presented in chapter three. In chapter four some catalyst properties of zeolite are introduced.

In the applied part, process descriptions of benzene and cumene units of Borealis aromatics production are first presented. The most likely and challenging impurities of benzene in Borealis' aromatics plant are discussed in chapter six. The requirements for benzene quality are determined by the cumene unit, mostly by the alkylation catalyst. These requirements as well as risks and effects of the impurities in the cumene unit are also introduced.

The main goal of the applied part is to find more efficient way to process benzene. Three different processing scenarios for benzene are compared with the current process. Simulations of the final benzene distillation in the benzene unit are carried out to gain information about the behavior of some components and to support the selection of the processing method. Also, some laboratory tests are conducted to study the efficiency of the clay treating of benzene as there is not any information about the performance of the clay now. Some new clay samples from other vendors are tested. Economical calculations, both capital expenditures and operating expenses, of the three process alternatives are conducted. Net present value, internal rate of return, and payback period for all the scenarios are calculated. According to simulations, laboratory tests, and calculations, recommendations are made for the processing method of benzene in Borealis' aromatics plant.

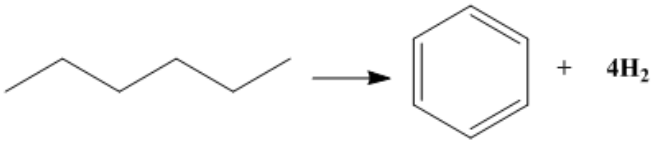
LITERATURE PART

2 Processes for benzene production

There are several methods to produce benzene from different feedstocks. In large scale production, the most used processes are catalytic reforming, benzene production from toluene, and steam cracking. These production methods are introduced.

2.1 Catalytic reforming

Catalytic reforming is a process in which straight chain hydrocarbons from gasoline or naphtha fractions ranging from C_6 to C_8 are converted into compounds containing aromatic rings. Catalytic reforming is widely used to produce benzene and other aromatics. The reactions taking place in the catalytic reforming process are dehydrogenation of cycloparaffins, dehydroisomerization of alkyl cyclopentanes, and cyclization and subsequent dehydrogenation of paraffins. (Fruscella 2000; Clark 2004) As an example, dehydrogenation of hexane is presented in equation (1). Hydrogen is formed as a by-product.



(1)

The operating conditions of the reformer as well as the feedstock type determine the amount of benzene produced. The feedstock to the reactor may be straight-run, hydrocracked, or thermally cracked naphtha fraction or gasoline fractions with hydrogen. If benzene is the most preferable product, a narrow naphtha cut of 71–104 ^{o}C is fed to the catalytic reformer. (Fruscella 2000) The catalyst used in the reforming is usually platinum mixture on a high surface area alumina or silica support. Rhodium, palladium, or rhenium is used in the platinum mixture. (Burdick

and Laffler 2010; Fruscella 2000) With the platinum catalyst the reforming process is called platforming which is probably the most widely used reforming technique. (Clark 2004)

In the platforming process a straight-run thermally cracked, catalytically cracked, or hydrocracked C_6 to 200 °C naphtha is used as a feedstock. The feedstock must be pretreated with hydrogen to remove sulfur, nitrogen, and oxygen compounds that would foul the catalyst and to remove any olefins from the feed. The feed is then mixed with hydrogen and preheated to 495–525 °C at pressure of 0.8–5 MPa. The hydrogen ratio in the feed should be 700–1400 m^3 hydrogen per m^3 of the feed. The feed is then led to the stacked series of reactors, usually three or four reactors. The catalyst pellets are usually supported by ceramic spheres. Two types of platforming processes are used: semi-regenerative and continuous platforming. In the semi-regenerative process the catalyst is regenerated in every 6–12 months. Time period for catalyst regeneration depends highly on the feedstock, process conditions and catalyst type. In continuous process, part of the catalyst is continuously flowing in cycles through the reactor and a regenerator. In the regenerator coke is burned off and the catalyst is activated again. After the reactors the product flow contains excess hydrogen and the aromatics. Hydrogen is then separated and liquid product is sent to a stabilizer where light hydrocarbons are removed. The bottom of the stabilizer, consisting of benzene, toluene, and non-aromatic (aliphatic) compounds, is then solvent extracted. (Folkins 2000; Fruscella 2000) The flow diagram of the platforming process is presented in Figure 1.

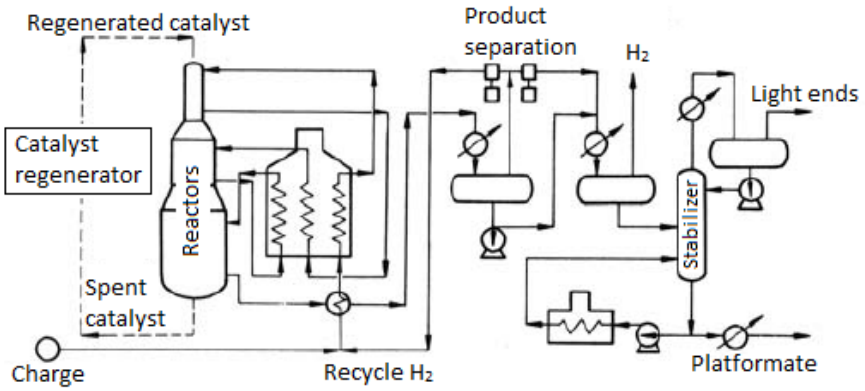


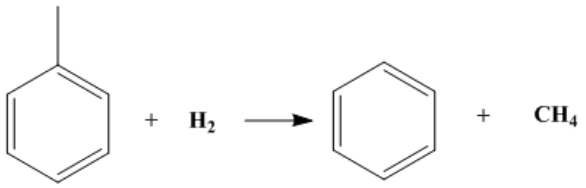
Figure 1. Catalytic reforming: the platforming process flow diagram (Fruscella 2000).

2.2 Benzene from toluene

Toluene is a by-product in catalytic reforming as well as in olefin plants cracking naphtha or gas oil. Usually supply of toluene is greater than is needed in industry. (Burdick and Laffler 2010) Depending on demand and market price of benzene and toluene the production amounts can be varied with different methods. The amount of toluene is reduced and the amount of benzene is increased by hydrodealkylation, disproportionation, and transalkylation of toluene. (Folkins 2000) These methods are presented next.

2.2.1 Hydrodealkylation of toluene

In hydrodealkylation process the alkyl group of molecule is replaced by hydrogen. In case of toluene, the methyl group is replaced by hydrogen to form benzene. (Burdick and Laffler 2010) The hydrodealkylation process is either catalytic or thermal. (Fruscella 2000) The catalytic processes take place over a hydrogenation-dehydrogenation catalyst such as nickel (Matar and Hatch 2001). Also platinum, platinum oxides, chromium oxides or molybdenum oxides on for example silica or alumina support are used (Fruscella 2000). The hydrodealkylation reaction is presented in equation (2) (Matar and Hatch 2001).



(2)

The catalytic Detol process developed by Air Products & Chemicals is one of the most widely used. In the process, toluene is mixed with hydrogen and the mixture is heated and pressurized before leading it to the reactor. The reactor is a column packed with fixed-bed catalyst. In the reactor the methyl group is split from the ring and a hydrogen atom replaces it. A hydrogen atom attaches to the methyl group and methane is formed. The operating temperature of Detol process is 500–595 °C and the pressure ranges from 4 to 6 MPa. The reaction is exothermic and the temperature is controlled by recycling cold hydrogen. The process consists usually of more than one reactor in series. The product gas and hydrogen are separated in high pressure flash drum. The product gas is condensed and pumped to stabilizer, where fuel gases are separated. The bottoms of the stabilizer are then clay treated and led to a column where benzene is distilled overhead. (Folkins 2000; Fruscella 2000) Benzene from Detol process is usually highly pure, up to 99.95 %. Some side reactions, such as hydrocracking and hydrogenation, might occur during the process and produce small amounts of light hydrocarbons and eliminate sulfur components. (Folkins 2000) The process flow diagram of the Detol process is shown in Figure 2.

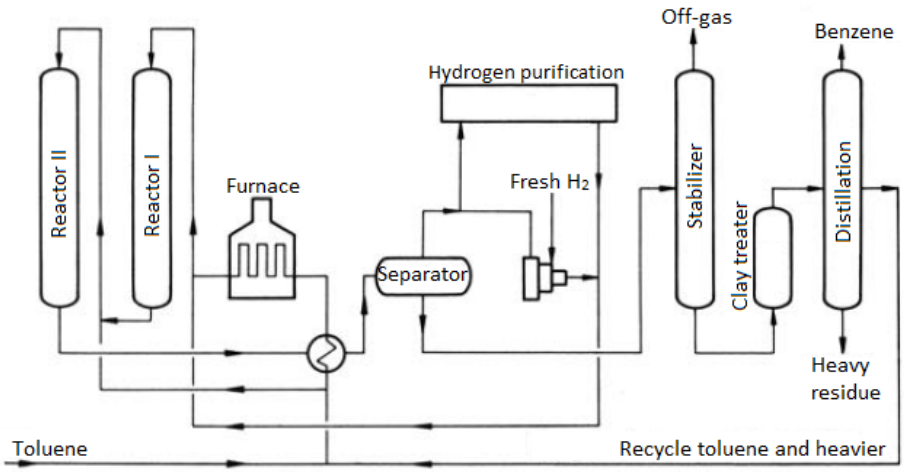
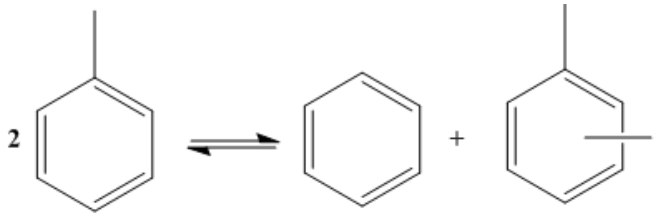


Figure 2. Hydrodealkylation of toluene: the Detol process flow diagram. (Fruscella 2000).

In thermal processes the systems are similar to the catalytic ones but operating temperature and pressure are higher: 600–660 °C and 3.45–6.9 MPa. Two mostly used processes are HDA process by Arco and Hydrocarbon Research, and THD process by Gulf Oil. (Folkins 2000) The yield of benzene in hydrodealkylation processes is up to 96–98 % (Burdick and Laffler 2010). Conversion is usually around 90 % and the benzene selectivity reaches over 95 %. Even though the conditions of the catalytic processes are milder and the selectivity is higher compared to the thermal processes the disadvantage of the catalytic process is the frequent regeneration need of the catalyst (Fruscella 2000).

2.2.2 Disproportionation of toluene

In a disproportionation reaction two toluene molecules are converted into one benzene molecule and one xylene molecule. The xylene can be any of the three isomers: *ortho*-, *meta*-, or *para*-xylene, shown in Figure 3. (Fruscella 2000) The reaction is presented in equation (3) (Matar and Hatch 2001).



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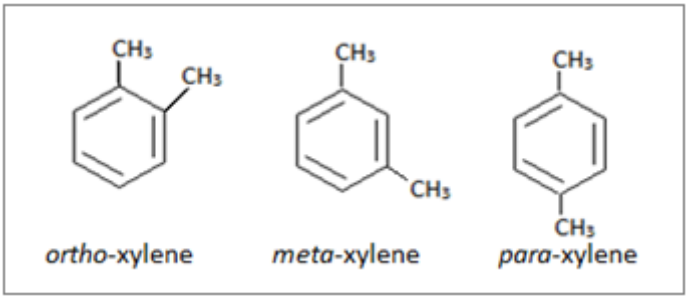


Figure 3. Xylene isomers (Folkins 2000).

Tatoray process by UOP for disproportionation of toluene is one of the most widely used. In that process, toluene stream is fed with high hydrogen recycle rate over a

catalyst. (Folkins 2000; Fruscella 2000) The hydrogen-toluene ratio should be from 5:1 to 12:1 (Fruscella 2000). The hydrogen is fed to the reactor to minimize the coke formation on the catalyst. The catalyst used is a noble metal, like platinum or palladium or rare earth metal, such as cerium or neodymium (Burdick and Laffler 2010; Folkins 2000). The reaction temperature is 350–525 °C and the pressure is 1–5 MPa. With pure toluene feed, yields of 41 w-% of benzene and 56 w-% of xylenes have been achieved. (Folkins 2000; Fruscella 2000)

In Figure 4, the process flow diagram of the Tatoray process is presented. The feed is preheated and vaporized before leading it to the top of the fixed bed reactor from where it down-flows through the catalyst. The reactor effluent is cooled after which the recycle gas is removed. The bottom of the separator is led to a stripper where C_5-overhead is removed. The bottom of the stripper, consisting of benzene, xylenes, and some toluene, is then sent to separation where it is clay treated and fractionated to produce high purity benzene and xylene. (Zukauskas 2006)

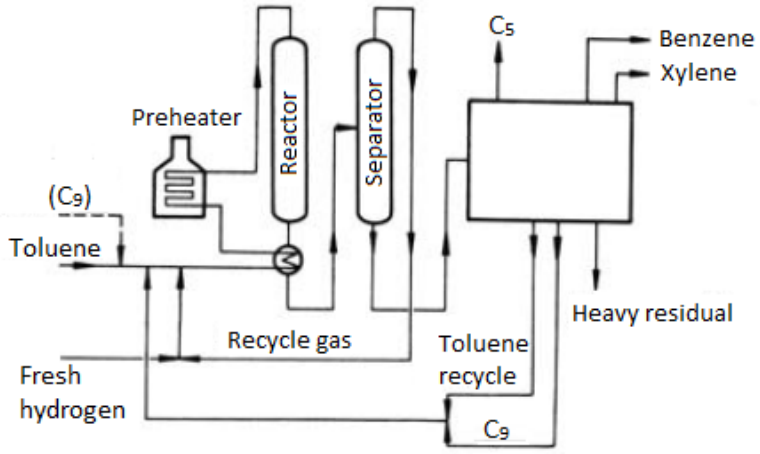


Figure 4. Disproportionation of toluene: the Tatoray process flow diagram. (Folkins 2000)

2.2.3 Transalkylation of toluene

Conversion of a mixture of toluene and C_9-aromatics into xylenes is called transalkylation. Otherwise the transalkylation processes are similar to disproportionation processes. The Tatoray process described above is used also for transalkylation of toluene. (Zukauskas 2006) For Tatoray process a feed mixture of

70 w-% of toluene and 30 w-% of C_9-aromatics has yielded 62 w-% of xylenes, 30 w-% of benzene, and 2 w-% of ethylbenzene. Thus, the more C_9-aromatics in feed, the larger the xylene yield is. (Folkins 2000)

2.3 Steam cracking

Pyrolysis gasoline is a by-product from steam cracking of heavy naphthas or light hydrocarbons like propane or butane. Pyrolysis gasoline is rich in aromatics, around 65 w-%, of which about half is usually benzene. (Fruscella 2000) The composition of pyrolysis gasoline depends on feedstock and the cracking severity. The more severe the cracking is, the more benzene the pyrolysis gasoline contains. Thus, the benzene content of pyrolysis gasoline ranges from 24 to 43 %. High temperature needed in ethylene production causes pyrolysis gasoline to contain diolefins and other unsaturated components. Diolefin content of pyrolysis gasoline is usually over 5 %. (Folkins 2000) Benzene can be recovered from pyrolysis gasoline by fractionation, solvent extraction, and distillation. (Folkins 2000; Fruscella 2000)

Pyrolysis gasoline needs to be pretreated before extraction to remove impurities like dienes, olefins, and sulfur compounds. A two-stage hydrotreating is an often used method. In the first stage dienes are hydrogenated to olefins. In the second hydrogenation stage olefins are saturated and sulfur compounds are removed. The conditions must be mild enough to prevent saturation of aromatics. In the diolefin removal both base-metal and noble-metal catalysts are used. In the olefin and sulfur removal nickel-molybdate and cobalt-molybdate catalysts are employed. In the diolefin operations the temperature is between 30 and 175 °C depending on the catalyst and the pressure is 2–6 MPa. (Folkins 2000)

After the hydrogenation different fractions must be separated. The separation method is selected according to the products wanted and the composition of the feed. (Folkins 2000) Usually in benzene production, lighter components, $\leq C_5$, are first distilled overhead, after which heavier, $\geq C_7$, components are separated to the bottom of the next distillation column. This leaves components with boiling point close to benzene and components that form azeotropes that cannot be separated by

distillation. For example solvent extraction and extractive distillation can be used for separation. (Burdick and Laffler 2010) We can see that the boiling points of C_6-C_9 hydrocarbons are close to each other. Letter P stands for iso- and normal paraffins, C for C_5- and C_6-cycloparaffins, and A for aromatics in Figure 5. (Sweeney and Bryan 2007)

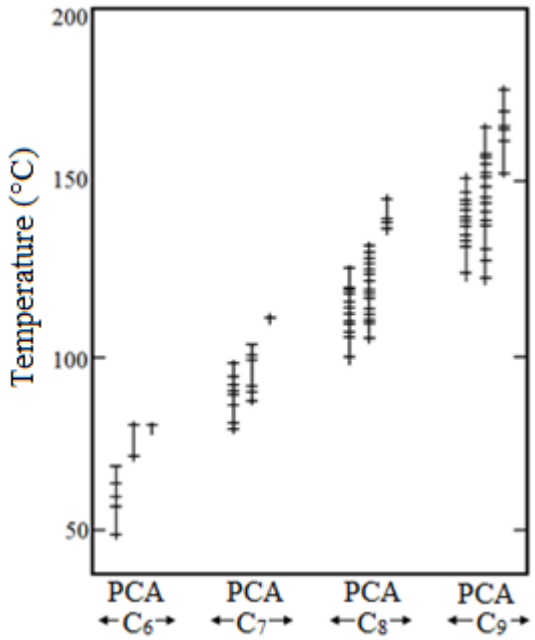


Figure 5. Boiling points of C_6-C_9 hydrocarbons (Sweeney and Bryan 2007).

Solvent extraction is often used for those mixtures that cannot be separated by distillation. For example the product flow from platforming process is usually processed by solvent extraction as well as the flow from hydrogenation/separation described above. There are numerous solvents used in the benzene separation: diethylene glycol, N-methylpyrrolidone, N,N-dimethylformamide, liquid SO_2, tetramethylene sulfone, and tetraethylene glycol (Furcella 2000). The separation methods are described more detailed in the next chapter.

3 Benzene separation and purification methods

Impurities in benzene have long caused problems in benzene utilization. According to Kadish et al. (1989) common impurities in benzene are water, thiophene, toluene, cyclohexane, methylcyclohexane, heptanes, saturated hydrocarbons, hydrogen sulfide, and sulfur oxide. Close-boiling hydrocarbons cause problems with separation by distillation so alternative separation methods must be used. Mostly used methods are extractive distillation, liquid-liquid extraction, and azeotropic distillation. To remove some trace impurities, such as olefins and nitrogen or sulfur compounds clay treating have been used. These separation and purification methods are presented next.

3.1 Extractive distillation

Extractive distillation is used to separate aromatics from crude benzene, toluene, and xylene (BTX) feeds. It is based on high-boiling solvent having considerable solubility for aromatics and little or no solubility for paraffins and naphtenes. This way these non-aromatic compounds can be distilled overhead and the aromatic-rich solvent is a bottom product. The solvent and the aromatics are then separated by distillation or stripping. (Folkins 2000)

3.1.1 Morphylane process

N-formylmorpholine (NFM) (Figure 6) is probably the most commonly used solvent in benzene extractive distillation as it changes the vapor-liquid equilibrium of the mixture. (Folkins 2000) Krupp Koppers developed in 1960s the Morphylane process which uses NFM as a solvent. Different molecular groups on both sides of the NFM molecule have an electrical effect that makes the molecule act like a small dipole. The electrical effect acts on the double bonds of the hydrocarbons. The more double bonds in the molecule, the more difficult is to convert it from liquid to vapor. If benzene and some other hydrocarbons are mixed with NFM to a ratio of 15 mol-% hydrocarbons: 85 mol-% NFM, the boiling point of benzene-NFM mixture is remarkably higher than for the other hydrocarbons. (Emmrich et al. 2001) Boiling

points of different hydrocarbons as pure components and mixed with NFM can be seen in Table 1.

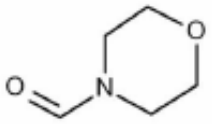


Figure 6. The N-formylmorpholine molecule.

Table 1. Boiling points of NFM mixtures (Emmrich et al. 2001).

Component	**NFM**	**Boiling point (°C)**	
15 mol-%	**85 mol-%**	**Pure component**	**Mixture**
2,2-dimethylpentane		79.19	83.43
2,4-dimethylpentane		80.49	84.74
2,2,3-trimethylbutane		80.88	85.21
N-heptane		98.43	103.15
Cyclohexane		80.72	87.39
Methylcyclohexane		100.93	109.55
Benzene		80.09	134

Thus, NFM makes the non-aromatic components, which boil above benzene, more volatile than benzene when extracted. In the Morphylane process NFM is fed to top of an extractive distillation column and preheated hydrocarbon mixture is fed to middle of the column. The flows contact each other countercurrent and benzene, and also toluene, is extracted to the solvent. Now non-aromatic components are distilled overhead and aromatic-rich solvent is fed from the bottom of the column to a stripper. In the stripper the aromatics are separated to the top of the column and NFM is recycled from bottom back to the extractive distillation column. A process flow diagram of the Morphylane process is presented in Figure 7. Benzene recovery from hydrogenated pyrolysis gasoline is 97 % and its purity is 99.95 w-%. (Folkins, 2000) However, according to Diehl et al. (2005) the aromatic yields of more than 99.9 w-% and purities of 99.999 w-% can be achieved with the Morphylane process.

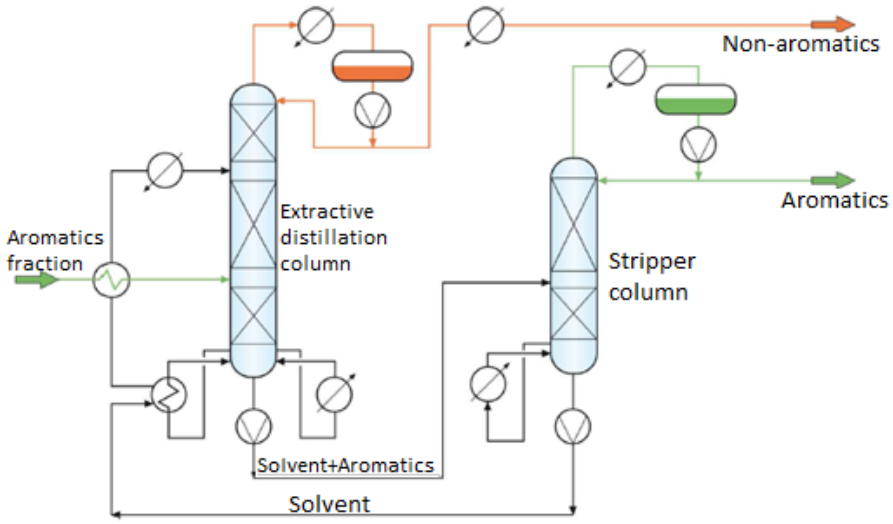


Figure 7. The Morphylane process by Uhde (Diehl et al. 2005).

3.1.2 Side rectifier arrangement and the single-column processes

Uhde has developed the Morphylane process further and has created a new extractive distillation technology. In this process there is one main column with a side rectifier instead of separate extractive distillation and stripper columns. Upper part of the main column corresponds an extractive distillation column. Bottom part of the main column together with the rectifier functions as a stripper column. Extract is recovered from vapor phase where the aromatics concentration is the richest. (Diehl et al. 2005)

As a next step of the extractive distillation, Uhde has created a single-column extractive distillation for aromatics recovery. In the single-shell process, side rectifier has been incorporated into the main column shell so that the process consists only of one column. Thermodynamic behavior of the side rectifier arrangement and the single-shell configuration are identical. (Diehl et al. 2005) An overview of the single-shell column is presented in Figure 8.

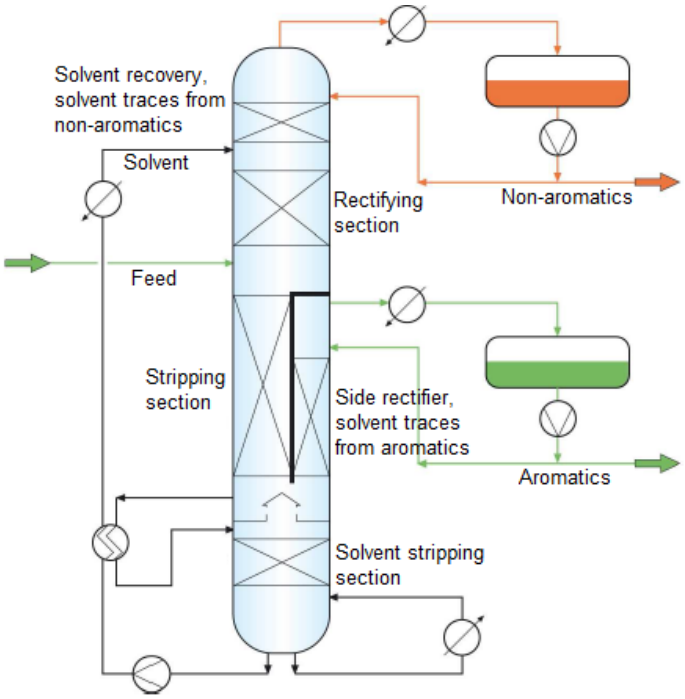


Figure 8. The single-shell process by Uhde (Diehl et al. 2005).

3.1.3 GT-BTX Select by GTC-Technologies

GTC-Technologies has developed an extractive distillation process, GT-BTX Select, to separate BTX from refinery or petrochemical aromatics streams like catalytic reformate or pyrolysis gasoline. (Anon. A 2016) Trade name for the solvent used in GT-BTX Select is Techtiv 500, which is a blend of solvent, co-solvent and additives. The process consists of two columns: an extractive distillation column and a solvent recovery column. In the extractive distillation column the solvent is led to top section of the column and aromatics containing feed is fed to middle section of the column so there is a countercurrent contact between the solvent and the feed. The aromatic-rich solvent is a bottom product. In the solvent recovery column the final aromatics are stripped out and the solvent is recovered for recycling. (Anon. B 2014) According to GTC Technologies (Anon. C 2013), the GT-BTX Select process is superior to many other extractive distillation processes in many aspects. For example, compared to Morphylane process, capacity, benzene loss in raffinate, and benzene purity are all better in the GT-BTX Select process. Also GT-BTX Select requires 7–12 % less steam than the Morphylane process. (Anon. C 2013)

3.2 Liquid-liquid extraction

Today extractive distillation has widely replaced liquid-liquid extraction in benzene processes. However, before extractive distillation liquid-liquid extraction was the most used separation process for aromatics. Solvents used in liquid-liquid extraction are usually high-boiling polar liquids. In general, they are fed to an extraction column from top section and hydrocarbons are fed from mid-section so the contact between solvent and hydrocarbons is countercurrent. Raffinate exits the column from the top and the aromatic-rich solvent from the bottom. Bottom product is fed to a distillation column, where the solvent is separated and recycled to the extraction column. There are several processes and solvents for benzene liquid-liquid extraction. (Folkins 2000) The most important ones are listed in Table 2 and described briefly next.

Table 2. Liquid-liquid extraction processes and solvents (Folkins 2000).

Process name	**Licenser**	**Solvent**
Udex	UOP-Down	Diethylene glycol
Sulfolane	Shell	Tetramethylene sulfone
Arosolvan	Lurgi	1-methyl-2-pyrrolidone
DMSO	IFP	Dimethyl sulfoxide
Formex	SNAM Progetti	N-formylmorpholine

Udex Process by UOP-Down uses diethylene glycol to extract aromatics from catalytic reformate, light oil, or pyrolysis gasoline. The glycol contains about 8 % water to increase aromatic selectivity from paraffins in the same boiling range. Feed temperature is around 65–150 °C. Recovery of benzene in extract is usually over 99 %. (Folkins 2000)

Sulfolane process developed by Shell uses tetramethylene sulfone as a solvent. The Sulfolane process has high selectivity and high yield and it has been the most used extraction process of aromatics. Thermal instability of the solvent can be overtaken by adding water to it. (Folkins 2000) Sulfolane is a water-soluble biodegradable and highly polar compound. (Matar and Hatch 2001) What is special in Sulfolane process is that any residual aromatics are returned to the extractor after extractive stripping of the extract. Yield of benzene is 99.9 %. (Folkins 2000)

Third liquid-liquid extraction process is Arosolvan Process by Lurgi, which uses 1-methyl-2-pyrrolidone (NMP) as a solvent. The water content of the solvent alters from 10 to 20 %. The process takes place in atmospheric pressure and temperature of 30–35 °C and it uses a low volume of the solvent. (Folkins 2000)

Dimethyl sulfoxide (DMSO) process developed by Institut Français du Pétrole takes place at ambient temperature and atmospheric pressure. In this process aromatics and paraffins are fed to the bottom of the extraction column, countercurrent to the solvent flow to combine reflux and backwash effects. The solvent is then recovered by re-extraction by paraffin solvent. The DMSO process has high selectivity for aromatics and it can be increased by adding water to the solvent. (Folkins 2000)

Snamprogetti's Formex process uses NFM mixed with water as a solvent. The process is designed to recover benzene, toluene, and xylene from BTX feed from catalytic reforming or hydrogenated pyrolysis gasoline. The extraction conditions are atmospheric pressure and temperature around 40 °C. Benzene yield from BTX feedstock is 100 %. (Folkins 2000)

3.3 Azeotropic distillation

Benzene forms minimum-boiling azeotropes with many alcohols and hydrocarbons. It forms also ternary azeotropes. In Table 3, some binary azeotropic mixtures of benzene are presented. (Fruscella 2000)

Table 3. Binary azeotropes of benzene (Fruscella 2000)

		Azeotrope	
Component	**Bp (°C)**	**Bp (°C)**	**w-% benzene**
cyclohexane	80.75	77.56	51.9
cyclohexene	82.1	78.9	64.7
methylcyclopentane	71.8	71.5	9.4
n-heptane	98.4	80.1	99.3
2,2-dimethylpentane	79.1	75.85	46.3
2,2,4-trimethylpentane	99.2	80.1	97.7
methanol	64.72	57.50	60.9
ethanol	78.3	68.24	67.6
2-propanol	82.45	71.92	66.7
2-butanol	99.5	78.5	84.6
tert-butyl alcohol	82.9	73.95	63.4
water	100	69.25	91.17

Naphtenes and paraffins can be separated from benzene and other aromatics by azeotropic distillation. (Folkins 2000) Heterogeneous azeotropic distillation is conducted by using an entrainer, which forms azeotropes with other components in the mixture and creates two immiscible liquid phases that can be separated by distillation. (Doherty and Knapp 2004)

Azeotropes can also be separated by homogeneous azeotropic distillation using an addition agent which is a high boiling liquid. The function of the agent is to alter the relative volatility of the mixture. For example, minimum boiling homogeneous azeotrope mixture of cyclohexane and benzene can be separated by adding acetone as a separating agent. Acetone forms a minimum boiling azeotrope with cyclohexane. This divides the desired pure components, benzene and cyclohexane, to different distillation regions and benzene can be recovered as a bottom product of a distillation. Cyclohexane and acetone can be separated by extracting with water, and finally acetone and water can be distilled apart. (Doherty and Knapp 2004)

3.4 Clay treating

Different clays, mostly acid-activated bentonites, are used in several benzene production processes to remove some components by adsorption. Clays are used for example to remove trace olefins or trace organic nitrogen compounds, and to comply with color specifications. (Netzer and Ghalayini 2002) Formerly clays were widely

used to remove diolefinic materials but the process is outdated due to poor efficiency and disposal problems (Folkins 2000). Basics of adsorption purification are presented next. Also clay used for purification purpose is introduced in this chapter as well as a few commercial clays and patents.

3.4.1 Adsorption purification

Clay purification is based on adsorption. Adsorption is a sorption operation, in which certain components of a fluid phase are selectively transferred to insoluble particles. The adsorption process is based on natural tendency of fluid components to collect at surface of a microporous solid material. The adsorbent should provide selectivity and capacity required for the separation or purification. Usually in the adsorptive separation processes, selectivity is provided by physical adsorption equilibrium. The adsorbing forces depend on the nature of the adsorbing molecule and the surface properties of the adsorbent. High capacity of adsorbent is obtained by using microporous materials with a high specific area, typically in the range of 300–1200 m^2/g. Such a large area is possible by combining particle porosity between 30 and 85 vol-% and average pore diameters from 1 to 20 nm. (De Haan and Bosch 2013)

In industrial applications four types of adsorbents are most widely used: activated carbon, silica gel, activated alumina, and molecular sieve zeolites. Activated carbons are generally used to remove hydrophobic organic species from gas and aqueous liquids. Silica gels are often used for removing water from various gases and also sometimes for hydrocarbon separations. As for activated alumina, it has high affinity for water and is often used for drying of various gases. Zeolites are often chosen when for example very high water removal is necessary. (De Haan and Bosch 2013) Apart from these four adsorbents, clays are also important adsorbents in industrial separation and purification. Especially differently processed clays are used in several applications. One great advantage of clays is that they are relatively cheap compared to many other adsorbents. (Murray 2014)

3.4.2 Introduction of clays

In this thesis with term clay is referred to natural earthy, fine-grained materials that comprise of a group of crystalline minerals, clay minerals. These minerals are hydrous minerals composing mainly of silica, alumina, and water. Many of the clay minerals contain also significant quantities of iron, alkaline, and alkaline earths. The uses and properties of clay depend on clay mineral composition, non-clay mineral composition, presence of organic material, type and amount of exchangeable ions and salts, and texture. The major clay mineral groups are kaolins, smectites, illites, chlorites, and palygorskite-sepiolite. Clays are abundant natural raw materials with variety of uses and physical properties. Clay deposits comprise either pure concentrations of particular clay mineral or mixture of clay minerals. (Murray 2014; Murray 2006)

In purification applications of petrochemicals, bentonite is the mostly used clay, and therefore it is the one introduced more detailed here. Bentonite is a rock which major constituent is smectite minerals. Smectite is a group of sodium, calcium, magnesium, iron, and lithium aluminum silicates. The group includes clay minerals of sodium montmorillonite, calcium montmorillonite, nontronite, saponite, and hectorite. Bentonites, in which the smectite sodium montmorillonite is the dominant mineral component, have a high swelling capacity. Largest deposits of this kind of high swelling clay are located in South Dakota, Wyoming, and Montana. The non-clay minerals in this bentonite are quartz, opal CT, zeolite, feldspar, and mica. Bentonites in which calcium montmorillonite is the major mineral component have usually low swelling capacity. Largest deposits of these clays are in Mississippi and Texas. In this bentonite quartz, opal CT, feldspar, and mica are the major non-clay minerals. World's mine production of bentonite in 2012 was 10 million tons, of which almost half was in United States. (Murray 2014)

Structures of smectite minerals are comprised of two silica tetrahedral sheets and one central alumina octahedral sheet (Figure 9a). The structure has an unbalanced charge because of substitution of aluminum for silicon in the tetrahedral sheet and iron and magnesium for aluminum in the octahedral sheet. Cations with water molecules enter

the layers in order to balance the negative charge. The ions in the structure depend on the clay mineral type. For example, sodium montmorillonite has sodium ions and water molecules in the interlayer and calcium montmorillonite has calcium ions and water molecules in the interlayer. Smectites expand when water or other polar molecules enter between the layers. (Murray 2014) A scanning electron micrograph of sodium montmorillionite is shown in Figure 9b.

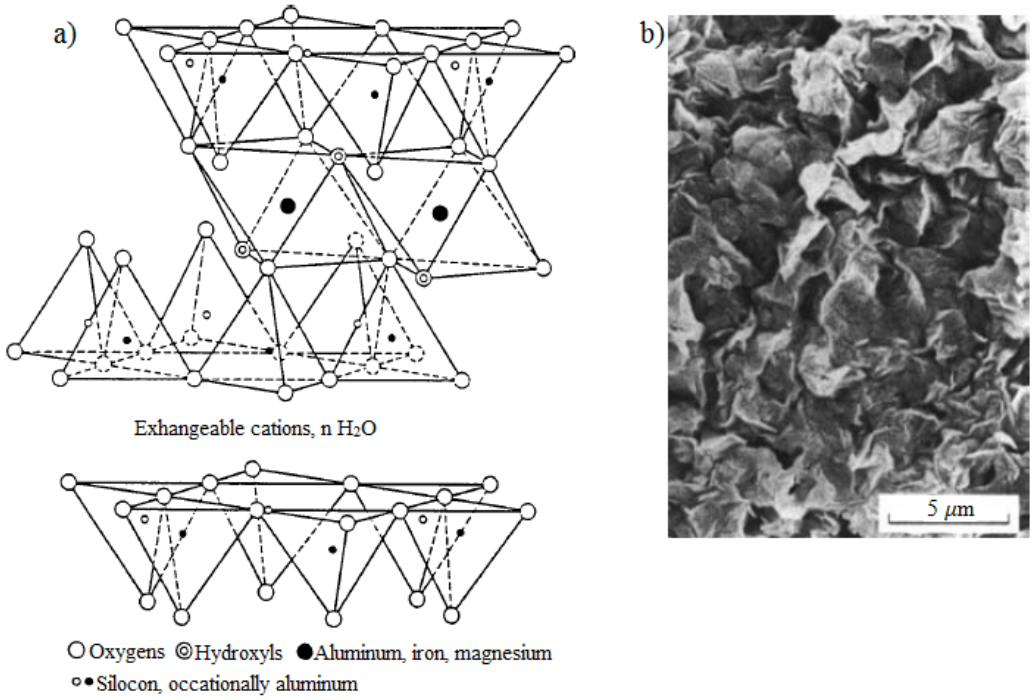


Figure 9. a) Diagrammatic sketch of the structure of smectite. b) Scanning electron micrograph of sodium montmorillionite. (Murray 2006)

Almost all bentonite is surface-mined. Processing of bentonite includes rather simple milling techniques that involve crushing, shredding, drying, grinding, and screening to suitable sizes. The high swelling sodium bentonites have moisture of less than 25 %. Processed bentonite generally contains only 7–8 % of moisture, although due to its hygroscopicity it may contain much more moisture when used. Granular bentonite is cracked using roll crusher and screened for proper size range of granular. Most powdered bentonite is ground with hammer or roll mills to < 90 % finer than 200 mesh.

Many industrially used bentonites are specially processed to create special products. Clay may be mixed with additives by extruder to improve viscosity and dispersion properties. Hydrophobic organic-clad bentonite is processed by replacing inorganic exchangeable ions with alkylamine cations. These clays are used in paints, greases, oil-base drilling muds, and to gel organic liquids. Acid-activation is used to make special sorptive clays that are used for example in bleaching and decolorizing oils. Acid-activation process involves slurrying bentonite in warm water, removing grit by hydrocyclones, reacting the clay with either sulfuric or hydrochloric acid at elevated temperature, dewatering and rinsing, and flash drying and pulverization. A dry activation process is also used where concentrated sulfuric acid is added to the clay in a blender and the clay is pulverized and dried to ensure uniform distribution of the acid. Aluminum, magnesium, and iron octahedral ions are partially removed in acid-activation resulting in highly charged particles saturated with hydrogen ions. By acid activation, substantial reduction in bulk density of clay has been achieved. (Murray 2014; Murray 2006)

3.4.3 Commercial clays and patents

Süd-Chemie provides different clays for hydrocarbon purification. For example, Clay A CO series' clays are acid-activated bentonites that are meant for BTX purification. Clay A CO 616 clay is for benzene purification and it can be used to remove olefins and organic nitrogen compounds, residues or decomposition compounds from NFM or NMP solvents. The main metal component of Clay A CO 616 is aluminosilicate (aluminum oxide and silicon oxide). Its granule size is 0.25–1 mm. (Anon. D 2007) According to Süd-Chemie (Anon. D 2007), as low concentrations as 0.1–10 ppm of nitrogen containing components can be removed.

BASF provides also clays for petrochemical applications. Acid-activated bentonite clays are particularly for BTX purification. They are used for olefin and nitrogen removal. (Anon. E 2016) BASF's Selexsorb series' alumina adsorbents are for hydrocarbon applications. Selexsorb CD is for adsorbing polar organic compounds including oxygenated hydrocarbons, mercaptans, and nitrogen-based molecules. Also Selexsorb CDX is an alumina-based adsorbent suitable for liquid hydrocarbon feed

purification. It can be used for polar organic component removal as well as for variety of nitrogen, sulfur, and oxygen-based organic contaminant removal. (Anon. F 2016)

There are several patents for hydrocarbon and aromatics purification based on adsorption. For example, Süd-Chemie has a patent for hydrocarbon purification. Used material is acid-activated smectitic clay minerals, which are used for removing olefins from aromatics. The clay mineral contains at least 5 mill-equivalents/100 g of exchangeable Al^{3+} cations. Olefin impurities containing feedstock is fed through a solid bed reactor at temperature around 150–200 °C. The granular clay acts like a catalyst and transforms the olefins into higher boiling compounds that can be removed by distillation. (Hahn et al. 2000)

Apart from clay applications, there are also several patents for other adsorbents, for example molecular sieves. ExxonMobil possess a patent for hydrocarbon feed pretreatment, in which the feedstock is contacted with two different zeolite molecular sieves. The first molecular sieve has a SiO_2/Al_2O_2 ratio (explained in chapter 4.2) less than 5 or pore diameter at least 0.6 nm and the second molecular sieve has a SiO_2/Al_2O_2 ratio grater that 5 or pore diameter less than 0.6 nm. The first zeolite type is for example type A (LTA) or type X (FAU). The second zeolite is for example MCM-22, MOR, ZSM-5 or beta. (Smith 2009) Some zeolite types are described in next chapter. According to Smith (2009), by using two molecular sieves in series a wide range of polar compound can be removed. If the first adsorbent is more hydrophilic and the second is more hydrophobic, removal of full range of nitrogen containing compounds and other trace level of contaminants can be removed. (Smith 2009)

4 Zeolite as catalyst

Catalyst used in Borealis' cumene alkylation reactor is zeolite licensed by ExxonMobil. Structure, properties, and poisoning of zeolite catalysts in general are introduced next.

4.1 Framework structure

According to Broach et al. (2012) zeolites are generally described as crystalline hydrated aluminosilicates with a three-dimensional framework structure. The framework constructs of SiO_4 and AlO_4 tetrahedra linked to each other through oxygen ions. The structure is regularly channeled or interlinked voids depending on the structure type. Pore diameters are in micropore range, so they are under 2 nm. The diameters depend on the number of tetrahedra in a ring around the pores. The pores contain water molecules as well as cations, usually alkali metal or alkaline-earth metal ions, which balance the negative charge of the framework. The cations are mobile and can be exchanged. A regularity of the channels and apertures as well as the pore diameters of same magnitude as molecular diameters enables zeolites to function as shape-selective catalysts and as selective adsorbents. (Broach et al. 2012; Csicsery and Kiricsi 2003)

There are several types of framework structures of zeolites. Four common types are presented in Figure 10. LTA structure type of zeolite A (Figure 10a) consists of sodalite cages linked via cubic units to form a larger alpha-cavity with a shape of truncated cubo-octahedron. If the sodalite cages are linked by hexagonal prisms, faujasite (FAU) structure type results (Figure 10b). This way formed larger cavities are called supercages because of large diameters of ~1.2 nm. For mordenite (MOR) structure (Figure 10c), the pore system is two dimensional. 12-ring channels are in effect only one dimensional. The channel system for ZSM-5 zeolites, structure type MFI (Figure 10d), is more complex. In MFI, linear parallel 10-ring channels are linked together with zigzag-shaped continuous pores with 10-ring apertures perpendicular to the channels, resulting a three-dimensional channel system. (Broach et al. 2012)

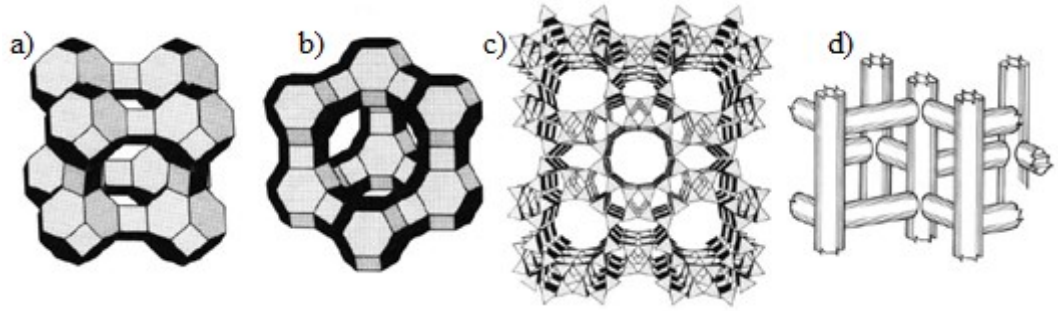


Figure 10. Framework structure of: a) Zeolite A (structure type LTA), b) Zeolites Y, X (type FAU), c) Mordenite (type MOR), d) ZSM-5 (type MFI) (Broach et al. 2012).

There are several suppliers that offer zeolite catalysts for liquid phase alkylation of benzene by propylene. Zeolite types for cumene production vary also depending on the supplier. For example, Dow-Kellog offers dealuminated mordenite zeolite catalyst, EniChem offers zeolite catalyst with beta structure, UOP provides zeolite with structure type Y, and ExxonMobil provides zeolite catalyst which structure is MCM-22. (Perego and Ingallina 2002; Cejka and Kubicka 2010; Csicsery and Kiricsi 2003) MCM-22 is a medium-pore zeolite with SiO_2/Al_2O_3 ratio typically around 10–20. (Tempelman et al. 2016) In MCM-22 framework structure there is 10 main windows, its channels are two-dimensional and the pore aperture size is 0.4 × 0.55 nm (Cejka and Kubicka 2010). MCM-22 has both 10- and 12-ring channels. These channel systems are not interconnected. (Csicsery and Kiricsi 2003) Main application of MCM-22 is benzene alkylation (Cejka and Kubicka 2010). It has been demonstrated that benzene does not enter the micro pores of the MCM-22. Rather it has been assumed that the alkylation reactions take place over Brønsted acid sites at the surface of the catalyst. (Sastre et al. 1999)

4.2 Properties of zeolites

Most of the chemical and physical properties of zeolites are determined by aluminum content of their framework. It is usually expressed by molar ratio of SiO_2/Al_2O_3. A ratio of < 2 is impossible, while according to Loewenstein rule, Al-O-Al groups cannot occur in crystalline aluminosilicates. The zeolites with SiO_2/Al_2O_3 ratio < 4 are classified as low-silica zeolites. Intermediate-silica is ratio of $4 < SiO_2/Al_2O_3 < 20$, and high-silica is ratio of $20 < SiO_2/Al_2O_3 < 200$. For example, surface selectivity depends on SiO_2/Al_2O_3 ratio. Alumino-rich zeolites preferably adsorb strongly polar

molecules, and hence are often used as drying agents, whereas increasing silicon content makes zeolites increasingly hydrophobic. The transition from hydrophilic to hydrophobic behavior occurs at SiO_2/Al_2O_3 ratio of ~20. The ratio defines also how strong acids zeolites tolerate. Low-silica zeolites are decomposed by strong acids. Acids dissolve the aluminum atoms out of the framework and the crystal structure breaks down. The higher the SiO_2/Al_2O_3 ratio is, the less sensitive the structure is for dealumination by acids. Aqueous alkalis lead to phase transition in high-aluminum zeolites, while very high-silica zeolites are dissolved by strong alkalis. (Broach et al. 2012)

As a catalyst, shape selectivity and strong acidity are the two dominant characteristics of zeolites. The properties that make zeolites capable to function as shape selective catalyst are: regularity of the pores and their apertures and the fact that the pores are in dimensions the same order of magnitude as molecular diameters. Thus, the shape selectivity occurs if the pores have similar dimensions as those of the molecules or transition states that take part to reactions. (Broach et al. 2012) There are three types of shape selectivity. The first is reactant selectivity, which limits the entrance of non-desired components by the shape or size of the molecules and favors the entrance of molecules that should react to the product molecule. The second is product selectivity, which limits the departure of the non-desired product molecules according to size and shape. The last form of shape selectivity is restricted transition state selectivity, which prevents some reactions to happen because of lack of space in the pores. (Csicsery and Kiricsi 2003)

The acidity of zeolite catalyst is either Brønsted or Lewis acidity. The acidity is a result of transformation of zeolite into hydrogen form, which makes them solid acids. Brønsted acid sites are protons attached to framework oxygen atoms, the number of which depends on SiO_2/Al_2O_3 ratio. If the framework contains more aluminum, the number of acidic OH-groups is decreased. However, then the strength of the remaining sites is increased. Lewis acidity is result of calcination of the hydrogen form zeolites, which causes decomposition of acidic hydroxyl groups and creates Lewis acid sites. In large scale industrial applications bifunctional catalysts in which

the acidity of zeolites is combined with the hydrogen-transferring function of noble metals are often used. (Broach et al. 2012)

4.3 Poisoning and deactivation of zeolite catalyst

A sorption poisoning of catalyst are often divided in two groups: irreversible and reversible poisoning. In reversible poisoning, spontaneous resumption of catalyst activity happens without separate regeneration when the poisonous materials are removed from the reagents. However, all sorption poisoning is essentially reversible. When classified as irreversible, the activity resumption of the catalyst only happens very slowly without regeneration. (Szabó et al. 1976)

Active sites of zeolite catalysts (acid, base, metal etc.) can be poisoned during the reactions decreasing the catalyst activity and often the selectivity too. Deactivation results from strong chemisorption of impurities in the feed on the catalytic sites. Other form of deactivation is coke formation on the catalyst surface or pores, blocking the access of reagent molecules to the active sites of the catalyst. There are also other effects of poisons apart from mere coverage of active sites: electronic modification of nearby metal atoms changing their chemisorption properties; restructuring of the surface by strongly adsorbed poison changing the catalytic properties for structure sensitive reactions such as hydrogenolysis; and inhibition or limitation of surface diffusion of chemisorbed species decreasing the probability of combination. The most common feed impurity poisons for acid and noble metal zeolite catalysts are nitrogen containing bases and sulfur containing compounds. (Guisnet and Ribeiro 2011) Twigg (1989) suggests the major zeolite catalyst poisons to be sodium, ammonia, and organic bases. Trimm (1997) as well says that organic bases for acidic catalysts or sulfur compounds for metal containing catalysts are the best known examples of catalyst poisoning.

Thus, for acid zeolite catalysts organic nitrogen bases and ammonia are common poisons. These nitrogen containing basic components not only poison the zeolite but also contribute to coke formation leading to additional deactivating effect. An additional harm of coke caused by nitrogen compounds is formation of NO_x

emissions during coke combustion. Some typical nitrogen containing organic compounds in crude oil based feedstocks are pyrrole derivatives, pyridine derivatives, and amino compounds. It has been studied that the deactivating power of basic molecules is primarily determined by a balance between their bulkiness or size and their affinity. The effect of size of basic molecule has been demonstrated by experiments. Bulky nitrogen bases which cannot enter the micro pores of zeolite have only limited poisoning effect and only inhibit outer acid sites. This selective poisoning can also been used to improve the shape-selective properties of catalyst. (Guisnet and Ribeiro 2011)

APPLIED PART

5 Benzene and cumene units at aromatics plant of Borealis

At Borealis' aromatics plant phenol and acetone are produced as final products. The plant is divided in three units: benzene, cumene and phenol units. However, for this thesis, only the benzene and cumene units are substantial and the processes of these units are described next.

5.1 Benzene unit

At Borealis' benzene unit, benzene is produced by fractionation and separation processes of pyrolysis gasoline and reformate. The pyrolysis gasoline comes pretreated from Borealis' own cracking unit. After hydrogenation and distillation stages, benzene is separated by Morphylane process licensed by Krupp Uhde. Other feedstock stream to benzene unit comes from Neste refinery site. It is a C_6 fraction of reformate stream which consists mostly of benzene. The treated pyrolysis gasoline and the reformate streams are mixed in a tank from where the mixture is fed to the Morphylane section of the benzene unit. (Lindtman 2016)

Solvent used in the Morphylane process is NFM and the process consists of two columns: an extractive distillation column and a stripper. In the extractive distillation column benzene is extracted to NFM and the benzene-rich bottom product is led to the stripper. In the stripper the solvent is separated and recycled back as bottom product of the stripper to the extractive distillation column. Benzene is an overhead product of the stripper. (Diehl 2005) Very high purity benzene has been achieved by Morphylane process but in case that toluene has reached the extractive distillation stage of the unit, it will be in extract and ends up to the benzene product. To avoid toluene or possibly other heavy impurities ending up to cumene unit there is a distillation column after the stripper. The distillation column separates highly pure benzene as overhead product and toluene, with a possibility of NFM and its

decomposition products, is separated as bottom product. A simple flow diagram of the Borealis' benzene separation process is presented in Figure 11.

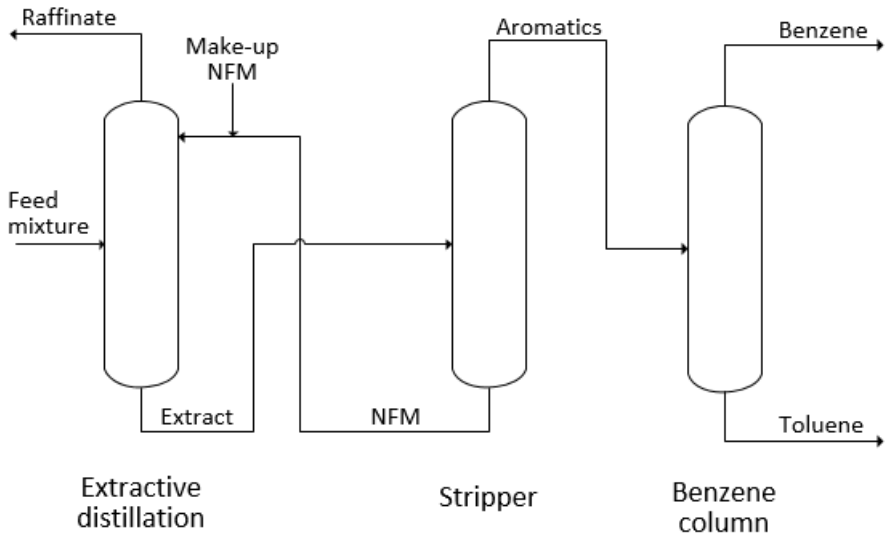
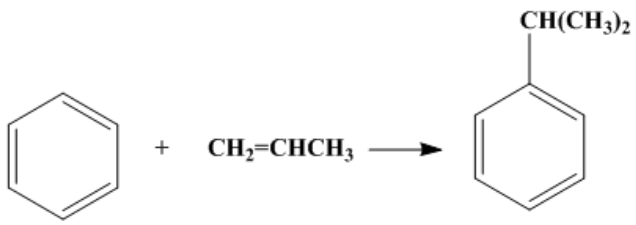


Figure 11. The benzene separation process of Borealis.

5.2 Cumene unit

Cumene is produced by process licensed by Mobil/Badger. Benzene is alkylated with propylene over ExxonMobil's zeolite catalyst resulting cumene according to reaction (4). Benzene used in cumene manufacturing is partly from Borealis' own benzene unit and partly imported. Propylene for alkylation originates from Neste's fluid catalytic cracking (FCC) unit.



(4)

The Mobil/Badger cumene process (Figure 12) starts from alkylation reactor, where premixed propylene and benzene react over a zeolite catalyst to form cumene. In the alkylation some polyisopropylbenzenes (PIPB) are formed. The alkylated stream is fed to depropanizer where propane originated from FCC-propylene feed is recovered

overhead as liquid petroleum gas (LPG). The bottom of depropanizer is fed to benzene recycle column from where some overhead benzene is fed to transalkylation reactor and rest is fed back to the alkylation reactor. The bottom product of the recycle column is fed to cumene column of which distillate is very pure cumene. The bottom product of the cumene column is distilled in PIPB column where the heavy aromatics and components are removed as bottom product. The overhead PIPB is then led to transalkylation reactor where benzene and PIPBs are transalkylated to cumene. The product stream from transalkylation is fed to benzene recycle column. (Hwang and Chen 2010)

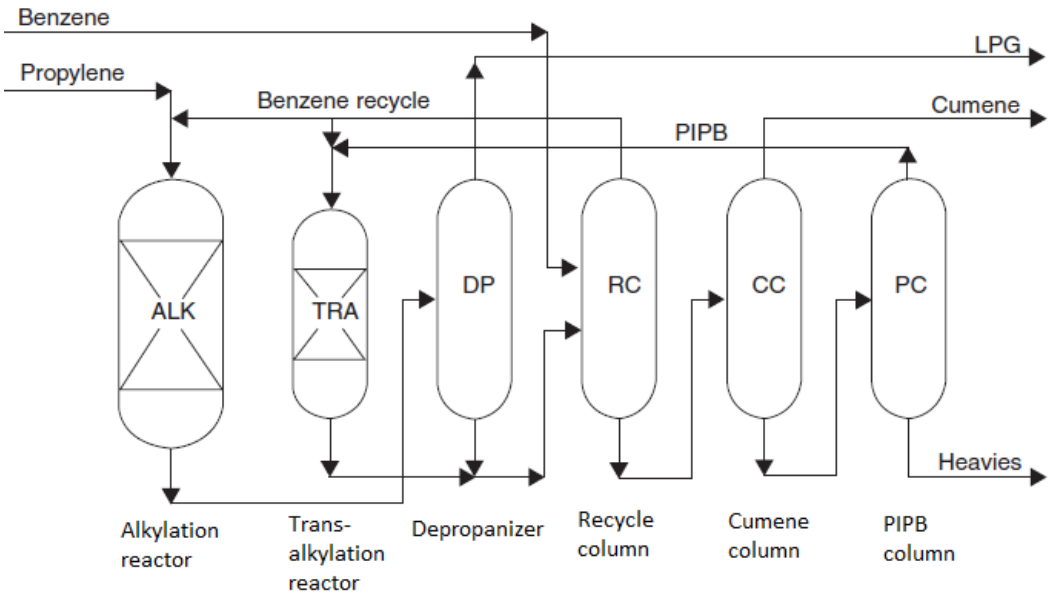


Figure 12. Mobil/Badger cumene production process (Hwang and Chen 2010).

6 Most likely impurities of benzene

There are many possible sources for impurities in benzene. As to impurities, the benzene specification for cumene process is very strict. Especially cumene catalyst is sensitive to any impurities in feedstocks, so the quality of benzene must be both high and stable. There are a few known impurities that have been assumed to cause problems with the cumene catalyst. Another concern is capacity limitation of cumene production. The impurities under consideration in this thesis are toluene,

methylcyclohexane (MCH), organic nitrogen components and trace olefins. The properties and behavior of these components are introduced next. There has also been evidence that impurities from imported benzene have caused catalyst deactivation in the cumene unit, so the importance of these impurities is also discussed in general in this chapter. Some physical properties of pure benzene, toluene, and MCH are presented in Table 4. In the end of this chapter there is a summary of all these impurities (Table 5).

Table 4. Some physical properties of benzene, toluene, and MCH.

Compound	Benzene	Toluene	MCH
Molecular mass (g/mol)	78.115	92.14	98.18
Boiling point (°C)	80.099	110.626	100.934
Melting point (°C)	5.533	-94.991	-126.593
Density (g/cm^3)	0.879	0.867	0.769
Heat of vaporization (kJ/mol) at 25 °C	33.899	38.26	35.383
Source	(Fruscella 2000)	(Folkins 2000; Ozokwelu 2014)	(Campbell 2011)

6.1 Toluene

In general, pyrolysis gasoline includes around 17–20 w-% toluene depending slightly on cracking severity. If the cracking severity increases, the toluene content reduces. In NFM extraction toluene is extracted to the solvent, as is benzene. (Folkins 2000) After separation of the solvent in a stripper, benzene and toluene can be separated by distillation due to the different boiling points, so that toluene is the bottom product. At the moment, distillation is the only option for toluene removal from benzene product. However, toluene should be removed from the process during the hydrogenation and distillation stages of the pyrolysis gasoline. The reformate stream though might include some toluene, if there has been some dysfunction in the unit. (Ouni 2016)

If toluene ends up in cumene alkylation reactor it will alkylate with propylene to form cymene. The alkylation produces a mixture of cymene isomers, *o-, m-,* and *p-*cymene. (Perego and Ingallina 2002) Around 73 % of toluene alkylates to cymene

isomers in the reactor. Thus, the main problem with toluene in the benzene feed is loss in cumene production. As toluene is the feedstock for hydrodealkylation and disproportionation processes in benzene manufacturing, it can be assumed that some toluene impurities might be in benzene product of these manufacturing methods.

6.2 Methyl cyclohexane

Methylcyclohexane (MCH), C_7H_{14}, in benzene might be a result of hydrogenation of small amount of toluene in benzene. (Campbell 2011) However, in the Borealis' benzene unit MCH usually comes from pyrolysis gasoline or reformate feedstocks. (Lindtman 2016)

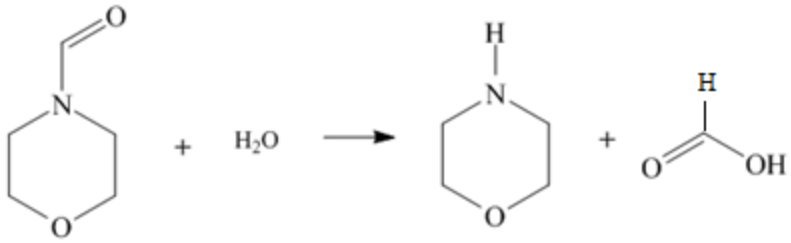
MCH is challenging to separate from benzene if it ends up to extractive distillation. Temperature of the extractive distillation must be high and constant so that MCH ends up into raffinate. If the temperature of the extractive distillation column drops even two to five degrees, MCH will be extracted to NFM. In the stripper as well as in the benzene distillation column, MCH will be an overhead product, as is benzene. Thus, MCH will end up to cumene unit and accumulates there. In the cumene unit MCH does not affect the process otherwise than constrict the capacity. (Lindtman 2016)

6.3 Solvent residues and decomposition product

In extractive benzene separation processes there is always a possibility for some impurities caused by solvent decomposition products or solvent residues in the product. For example, organic nitrogen contamination might occur when using NFM (Morphylane process) or NMP (Arosolvan process) as solvents in benzene extraction processes. (Netzer and Ghalayini 2002)

Nitrogen containing solvent decomposition products are extremely harmful to zeolite catalyst of alkylation in the cumene process. The basic components neutralize acidic active sites in the pores of the catalyst. (Guisnet and Ribeiro 2011) In the Borealis' cumene process the nitrogen impurities are NFM and morpholine. Morpholine comes

from the decomposition of NFM according to reaction (5), where also formic acid is formed. Apart from basic nitrogen component, acidic components are also poisonous for the catalyst. (Ouni 2016)



(5)

These nitrogen components are removed in the last distillation column of the benzene unit, the benzene column. There is also a cold clay treater prior to the cumene unit through which the benzene stream is always fed to remove basic nitrogen containing organic components. (Lindtman 2016)

6.4 Olefins

Olefins are cyclic or acyclic hydrocarbons that have one or more carbon-carbon double bond. Olefins come to the benzene unit from pyrolysis gasoline or from the reformate stream. Hydrogenation of pyrolysis gasoline should re-form the olefins to paraffins which are removed in extractive distillation. (Ouni 2016) Olefin content is monitored by bromine number, which tells the amount of bromine that will react with 100 g of the sample. Thus, it measures trace amounts of unsaturation in the material. (Nadkarni 2007)

If the olefins reach the extractive distillation, they will partly end up in the aromatic-rich extract. In this case, olefins can be removed by hot clay treater. If not removed, olefins cause color to the benzene product. In the alkylation reactor light olefins react and form undesirable side products and so limit the capacity of the cumene production. (Lindtman 2016; Ouni 2016)

6.5 General impurities affecting the catalyst

Apart from earlier described solvent decomposition products, there are several other impurities that are poisonous to the zeolite catalyst and deactivate it. Especially imported benzene might contain some random impurities which are hard to predict, and so it is challenging to be prepared for their purification.

Generally, harmful impurities for zeolite catalyst are basic components, especially nitrogen containing basic components, acids, sulfur containing basic components, oxygen containing or oxidizing components like methanol, and metals. Sulfur containing components in imported benzene are for example thiophene, COS, sulfolane, and sulfides. The possible oxidizing components are alcohols, ethers, and carbonyls. Some impurities deactivate the catalyst more permanently but some only momentarily. For example, after methanol contamination the catalyst deactivates only for a moment, but after a while it recovers partly again without separate regeneration. Some sulfur containing components have the same property. However, for example metals or alkali metals like arsenic, iron, sodium or calcium poison the catalyst irreversibly. (Wörlin 2016; Ouni 2016)

Table 5. Summary of the impurities.

Impurity	**Source**	**How to remove**	**Behavior in the process**	**Effect on the process**
Toluene	Pyrolysis gasoline, reformate	Distillation	Alkylates to cymene	Capacity limitation
Methylcyclo-hexane	Pyrolysis gasoline, reformate	Extractive distillation	Accumulates to the cumene unit	Capacity limitation
Basic organic nitrogen components	Solvent residue (NFM)/ decomposition product (morpholine)	Distillation, cold clay treating		Deactivation of the catalyst
Olefins	Pyrolysis gasoline, reformate	Hydrogenation, hot clay treating	Alkylates with benzene → not-desired byproducts	Color in benzene, capacity limitation
Other impurities - Basic nitrogen - Basic sulfur - Oxygen components - Acids - Metals	Imported benzene	Clay treating		Deactivation of the catalyst

7 Approach for techno-economic assessment

Techno-economic assessment combines process modeling and engineering design with economic evaluation. The aim is to provide both quantitative and qualitative understanding of the impacts that new technologies or technology changes have on the financial viability. (Wallace 2011)

Techno-economic assessment of this thesis consists of following steps:

- Collecting information of benzene impurities that are most harmful to cumene catalyst.
- Selecting scenarios for benzene processing.
- Simulation of benzene distillation column with Aspen Plus.
- Laboratory tests for clay samples to collect information about their performance.
- Evaluating investment needs for all the process scenarios.
- Operating cost evaluations for each scenario.
- Calculation of financial indicators: NPV, IRR, and PBP.
- Comparison of financial and technical viability of the scenarios.

8 Process alternatives

There are three different scenarios for benzene handling compared in this thesis that are described next. The main difference in these scenarios is the distillation of benzene. Three targets aspired by the scenarios are: to be able to source benzene with higher toluene content, to avoid distilling on-spec benzene, and to allow alkylation catalyst run length match turnaround interval. In the calculations and simulations benzene amounts of 5000 kg/h of imported benzene and 17400 kg/h of self-produced benzene are used. So, the total amount of benzene fed to the cumene unit is assumed to be 22400 kg/h which is the maximum amount of benzene used.

8.1 Scenario I: Distillation of all used benzene

In the first scenario all used benzene is distilled over, the self-produced as well as the imported. By distilling all used benzene there is a possibility to purchase lower quality benzene with lower price. This method would also ensure that all heavy compounds like toluene, solvent residues and other impurities would be removed and by that ensuring longer life for cumene alkylation catalyst. In this scenario, the

amount of benzene distilled over is 22400 kg/h. A block diagram of scenario I is presented in Figure 13.

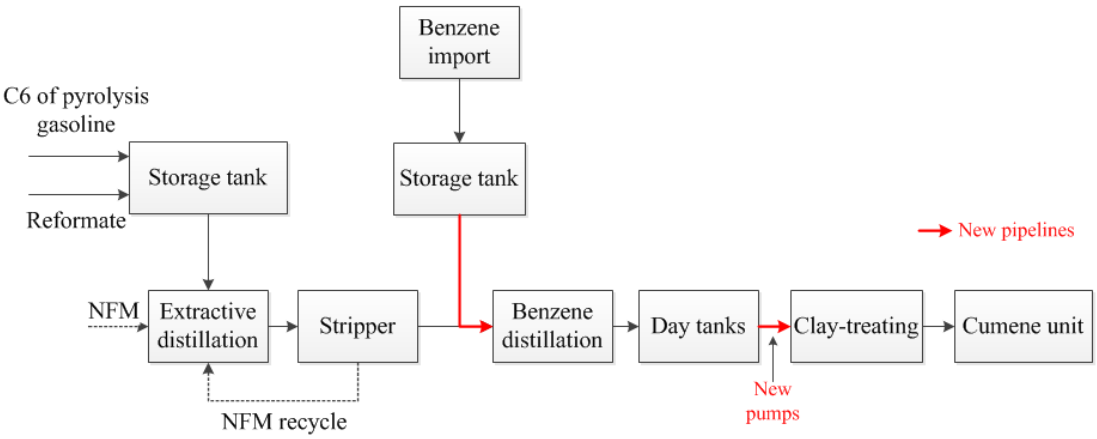


Figure 13. A block diagram of scenario I: distillation of all used benzene.

8.2 Scenario II: Distillation of imported benzene

The second scenario is to distil only the imported benzene and to bypass the distillation column for self-produced benzene. There rarely is an actual need for the distillation of the self-produced benzene while during normal operation it is on specification. For this scenario, removal of nitrogen containing basic compounds by clay treatment is however crucial. Distillation of imported benzene would also give an opportunity to source lower quality and cheaper benzene. This would also solve the problem of uncertainty of the contaminants in the imported benzene, at least for heavy impurities. The benzene column is all the time available for distillation of also self-produced benzene in case of toluene peaks or other impurities. So, an online analysis for the distillate of the stripper would be needed required. Both the self-produced as well as the purchased benzene would be clay treated for nitrogen compounds. In scenario II the amount of benzene distilled over is 5000 kg/h. A block diagram of scenario II is presented in Figure 14.

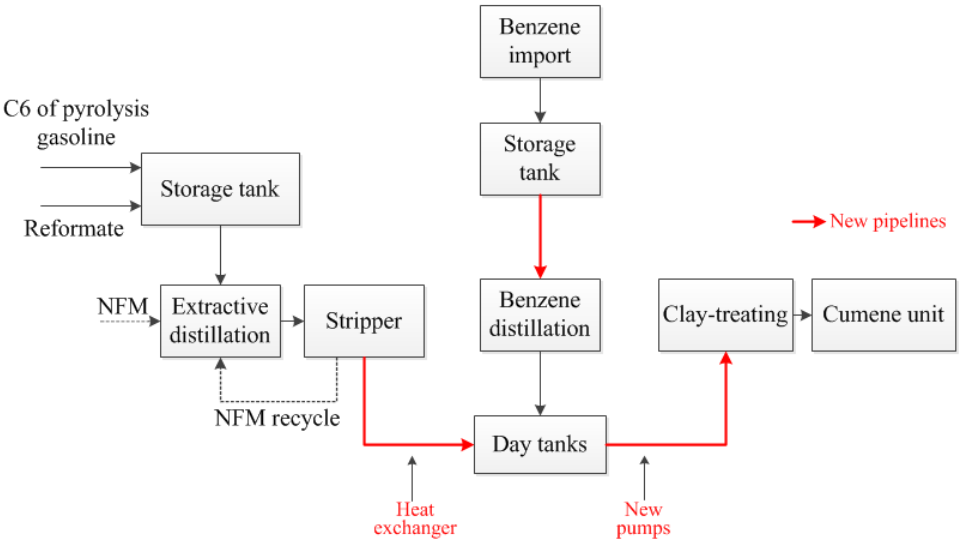


Figure 14. A block diagram of scenario II: Distillation of imported benzene.

8.3 Scenario III: Bypassing the benzene distillation column

The third scenario for benzene processing is bypassing the benzene distillation column completely. This means that the benzene from top of the stripper after the extractive distillation is fed straight to the storage tank. The imported benzene is also stored in the same tank. There is however always a chance for operation dysfunction, which might lead to contamination of the benzene product. These contaminants are the ones described in chapter 6. To ensure the benzene quality, clay treaters are used to remove at least nitrogen containing organic bases and possibly some olefins and impurities from imported benzene. However, if toluene ends up to the benzene product distillation is only option for removing it. MCH removal is not affected by bypassing the distillation while MCH distils over with benzene anyway. For this scenario, the distillation column must be all the time in stand-by mode for any incoming toluene and would need an online analysis for toluene. A block diagram of scenario III is presented in Figure 15.

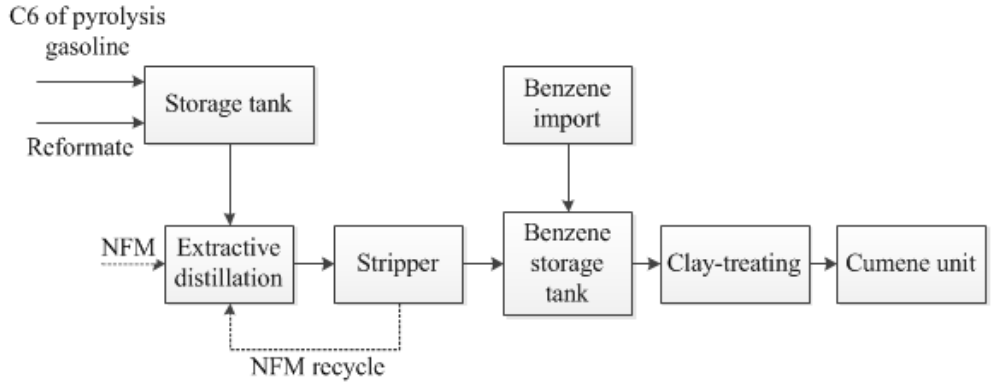


Figure 15. A block diagram of scenario III: bypassing the distillation column

9 Simulation of benzene distillation column

Initially two main objectives to be defined by simulations of the benzene distillation column were the maximum capacity of the column and the minimum capacity of the column. However, the limiting factor of the minimum capacity of the column turned out to be the column's reboiler that will cause hammering if the steam feed is too low. These capacity limitations are presented next.

9.1 Maximum capacity of the column

Aspen Plus V8.8 simulation program was used for simulation. UNIFAC was selected as VLE method because it can be used for predicting behavior of complex substances on the process according to their functional groups. The feed composition was 99.9 m-% of benzene, 946 ppm of toluene, 50 ppm of MCH, and 2 ppm of NFM and morpholine. Distillate to feed ratio was set for 0.9985. The used feed temperature was 75 °C. The maximum capacity was defined by flooding factor that must be less than one so that a column will function as it should. If the flooding factor rises above one, liquid flow in downcomers will be disturbed and trays in the bottom of the column will dry out. Flooding factors were simulated with different feed amounts and reflux ratios. The flooding factor simulation results are in Figure 16. R in the figure refers to reflux ratio.

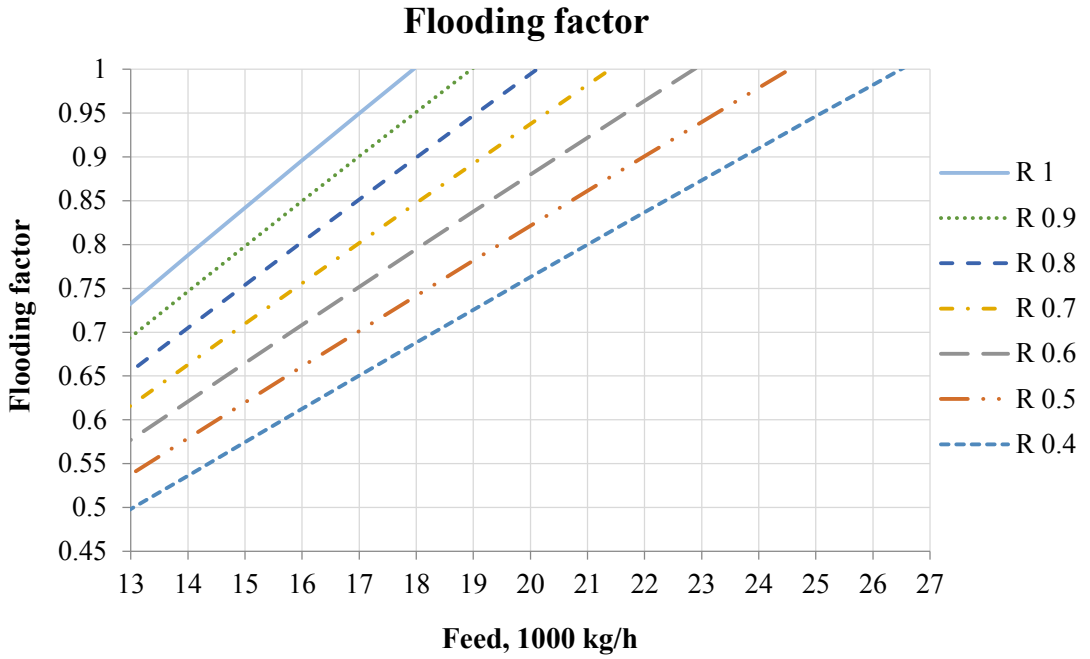


Figure 16. Flooding factors of the benzene distillation column.

According to the simulations, distillation of the feed in the scenario I is possible. This is the scenario where the feed amount is the greatest, 22400 kg/h. Thus, the maximum capacity of the column is enough at least when the reflux ratio is at most 0.6, as can be seen from the diagram in the Figure 16.

9.2 Minimum capacity of the column

The minimum capacity of the benzene distillation column is limited by the reboiler of the column. In order to avoid said hammering, the steam feed to the reboiler must be over 4000 kg/h. According to the simulations, the benzene feed amount must be 13000 kg/h with reflux ratio of 0.5 so that the steam consumption is sufficiently high. This means that scenario II, distillation of only imported benzene, would not be feasible without any changes to the process while the feed amount to the column is only 5000 kg/h in this scenario.

As a solution to the minimum capacity problem, redirecting of the condensate from the reboiler to a lower pressure condensate tank has been suggested. This would give

an opportunity to run the distillation column with smaller steam feed to the reboiler. Hence smaller feed amount to the column would be possible.

After the condensate redirecting, the minimum capacity of the column is determined by a turn down ratio the column. The turn down ratio is 40 % of maximum liquid loading on higher trays. A flow of 7500 kg/h in top section of the column is required which means a reflux ratio of 1.5 when the feed to the column is 5000 kg/h in the scenario II.

10 Clay treating performance

The clay treaters used at Borealis for benzene purification are introduced next. Also laboratory tests conducted as part of this thesis about clay treating are presented. Three different clays that were tested are introduced in Table 6. All three clays are acid activated bentonite. In this case, the main component to be removed from benzene is NFM, so the testing concentrated mainly on that. It is to be noted that all the three clays are initially designed for olefin purification from aromatics. However, they are also suitable for purification of basic nitrogen components because of acid activation.

Table 6. Clays for benzene purification.

	Clay A	**Clay B**	**Clay C**
Bulk density (kg/m^3)	720	870	940
Density (kg/m^3)	2600	2280	2280
Porosity (%)	72	62	59

10.1 Clay treater

Clay treater used at Borealis for benzene purification is a cold clay treater. It is operated at ambient temperature without any external heating or insulation. There are two clay towers that are operated one at a time. Towers are filled with clay and some filters and sands to prevent letting the clay to the process. Process stream is fed to top

of the tower and it flows through the clay bed by gravity and outflows from bottom of the tower.

Clay bed of one treater is 3.5 m^3 (height 3.3 m, diameter 1.2 m). The mass of the clay bed filled with clay A is 2520 kg. The mass flow used for calculating weight hourly space velocity (WHSV) for the clay treating is 22400 kg/h. WHSV is calculated by dividing the mass flow by the adsorbent mass. In this case the WHSV is 8.9. For calculations, the NFM concentration of benzene was assumed to be 2 ppm before the clay treating.

10.2 Laboratory tests

The adsorption capability and capacity of the clays for NFM removal were tested with two different test methods presented next. The adsorption ability of clay to adsorb some other components was also tested. The analyses were conducted with gas chromatography (GC). All the GC-results as well as a detailed description of performing the tests are presented in Appendices 1 and 2.

10.2.1 Adsorption capability tests for NFM removal

The adsorption tests were conducted to have information about changes in clay efficiency during a two hour test. The test equipment was a 70 ml glass column with a valve and water circulation. 5 g of clay was placed into the test equipment through which the test solution was drained by gravity. NFM concentration of the test solution was around 100 ppm. The flow velocity of 360 g/h was adjusted by the valve using a scale and a timer and the temperature was adjusted by the water circulation. The WHSV value of the test was 72. Clay performance was tested in three different temperatures (20, 30 and 40 °C). A sample of the test solution was taken and analyzed of the test solution before the clay treatment. The solution was drained through the clay bed for 15 minutes to a 100 ml sample bottle after which the bottle was switched to a new one. Eight sample bottles were collected from each test. A sample was taken from every other sample bottle and analyzed with GC. More detailed instructions for the adsorption test are in Appendix 2.

Several WHSV values with different NFM concentrations were tested with clay A before final testing values were decided. The following conditions were tested in temperature of 30 °C:

- WHSV 9, NFM concentration 10 ppm → no NFM through
- WHSV 9, NFM concentration 100 ppm → no NFM through
- WHSV 18, NFM concentration 10 ppm → no NFM through
- WHSV 36, NFM concentration 100 ppm → ~0.5 ppm NFM through
- WHSV 72, NFM concentration 100 ppm → NFM through

The results of the adsorption tests for all three clays are summarized in Figure 17. A repetition test was conducted for clay A in temperature of 30 °C. The results of the repeated test are very similar to those of the original test. Accurate GC results of the tests can be found in Appendix 1.

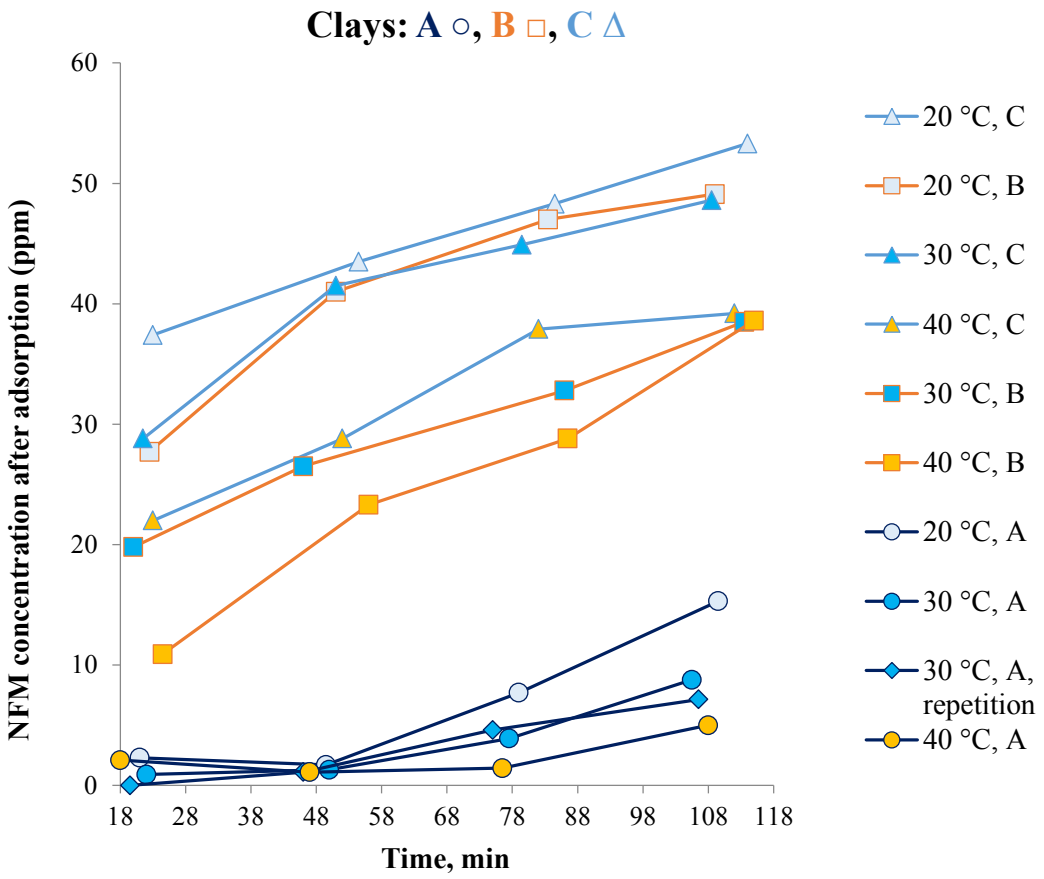


Figure 17. Adsorption capability test results.

According to the test results, it can be seen that adsorption capability for clay A is remarkably higher than it is for clay B and clay C. The adsorption capability of clay B is somewhat higher than it is for clay C. From the results it can also be seen that a rise in temperature enhance adsorption capability for all three clays, at least in temperature range of 20–40 °C.

10.2.2 Capacity tests for NFM removal

In capacity tests the adsorption capacity of the clays to remove NFM from benzene was tested with a 20 hour test. Test was conducted by adding 1 g of clay to about 425 g of benzene solution, which NFM concentration was known. The bottle was placed horizontally in a shaker to maximize the mixing of the clay and the solution. After 20 hours of shaking the bottle was placed vertically on a table and the clay was let set on the bottom. Then about 50 ml sample was taken and analyzed with GC. The test results of the capacity tests are presented in Table 7.

Table 7. Capacity test results.

	Solution mass (g)	**NFM mass in solution (g)**			**%**
		start	end	removed	removed
Clay A	426.5	0.151	0.040	0.111	73.6
Clay B	426.2	0.150	0.079	0.072	47.8
Clay C	426.0	0.149	0.097	0.052	35.0

The saturation times with different clays were calculated by the capacity tests. The feed of 22400 kg/h, NFM concentration of 2 ppm and clay bed volume of 3.5 m^3 were used in calculations. The calculation was conducted by multiplying the capacity test result of clay by the mass of that clay bed, and then determining how much feed with NFM concentration of 2 ppm would be needed for that amount of NFM. The saturation times are shown in Table 8.

Table 8. Saturation times for clay beds.

	Clay A	Clay B	Clay C
Clay bed mass (kg)	2520	3033	3274
Saturation time (hours)	6238	4864	3804
Saturation time (months)	8.7	6.8	5.3

10.2.3 Adsorption tests for other components

The ability of clay to adsorb methanol, phenol and 1-methyl-2-pyrrolidone (NMP) was also tested for clay A and clay B. The tests were performed the same way and with the same equipment as the adsorption capability tests for NFM. The amount of clay was 10 g and the liquid flow was 180 g/h. Temperature was 30 °C.

The tests showed that neither of the tested clays adsorbs methanol at all. As to phenol, both clays act similarly, initial adsorption followed by rapid desorption. After one hour of operation almost all phenol flows through. NMP however is adsorbed by both clays similar to the case with NFM. The GC-results of these tests are presented in Appendix 1.

10.3 Analysis methods

The analytical methods used for analyzing benzene impurities tested in the clay treating tests were gas chromatography and spectrophotometry. The analysis method used for determining NFM concentration as well as NMP concentration in benzene was GC using internal standard technique. The internal standard in this analysis is 9-ethylcarbazole. Methanol concentration was also analyzed with internal standard GC. This GC is used primary for olefin and aromatic hydrocarbon analysis from benzene. In the method, 1-fenylbutane is used as an internal standard.

Phenol in benzene was analyzed by spectrophotometer. The method is a chemical analysis method that is based on reactions between phenol and basic aminoantipyrine solution. The reactions will create red color, by which the concentration is determined. The spectrophotometer observes the waves through the colored solution column and gets transmittance as a ratio of light intensity after it passes through the

sample and the initial light intensity. There is a connection between absorption and concentration according to Lambert-Beer's law, which is used to determinate the concentration of a solution.

10.4 Qualitative error consideration

These tests were conducted in small scale in laboratory conditions. Compared to real process conditions there are many differences, such as turbulence in the clay tower, changes in flow velocity, differences in NFM concentration, different dimensions of the clay bed, and temperature and pressure changes. These differences in scale and conditions cause uncertainty to scale-up of the laboratory results to the process conditions. Also there is a possibility of human error in performance of the tests. For example, the flow velocity was adjusted with scale and timer and visually estimated to be correct, which causes inaccuracy.

The concentrations used in the tests were really low, only some parts per million. This low concentration is hard to analyze and there is a great probability of analyze errors. With GC, there is also a possibility of inaccuracy of the results due to injection technique.

A repetition test was however conducted to have certainty of the testing method. Results of the repetition test were very similar to those of the original test. Thus, it can be assumed that the testing method is reliable.

11 Financial calculations of the process alternatives

The financial evaluation of the process alternatives is conducted by calculating capital expenditure (CAPEX) and operating expenses (OPEX) for all three scenarios. Some financial indicators are also calculated and sensitivity analysis with different variables is conducted.

11.1 Investments

All the scenarios need new investments. Estimates for investment costs are calculated by purchase price estimate multiplied by different factors. Factors used in investment cost calculations are: engineering, procurement and construction management (EPCM); contingency factor, and cost index. The cost index for all investments is calculated based on inflation forecast for year 2020, which is 1.8 % in euro area (Anon. G). The cost index is calculated by equation (4):

$$(1+I)^n \rightarrow 1.018^4 = 1.074 \quad (4)$$

Where: I is the inflation rate
n is the number of years until the investment

Year 2020 is used because that is the earliest time the investments could be implemented. For pumps and heat exchanger a factor for total installation costs is also used. All the investment needs are described next and also listed in Appendix 3.

11.1.1 Investments in scenario I

Scenario I needs roughly 1080 m new pipeline. A new pipeline must be built from the tank of imported benzene to the benzene distillation column. Another pipeline, from benzene day tanks to the clay treaters is needed. All the pipelines are carbon steel and 3 inches in diameter. In purchase price estimation of pipe, apart from material cost the estimation includes also insulation, electrical heat tracing, steel supports, and scanning of the pipe as well as subcontracting costs. With all the factors, total cost for pipelines in the scenario I is 695000 €.

A pair of new pumps is also needed in scenario I. The new pumps are placed after the day tanks, so they pump all 22400 kg/h benzene which is fed to the cumene unit. Before the cumene unit, the stream flows through the clay towers where pressure is around 20 bars. As the maximum pressure need for the pump is placed 30 bars. The

cost estimation is based on data available from similar pumps purchased to the plant. The total cost estimate for the pumps is 565000 €.

Total costs for investments in the scenario I are 1260000 €.

11.1.2 Investments in scenario II

Scenario II needs around 1400 m new pipeline. A new line must be built from the tank of imported benzene to the benzene distillation column. Another line from benzene day tanks to the clay treaters is needed. A third new line must be built from the stripper column to the day tanks. All the pipelines are carbon steel and 3 inches in diameter. Factors and price are the same as was used for scenario I, so the cost estimate for pipelines in scenario II is 901000 €.

Also in scenario II, a pair of new pumps is needed. The pumps are the same as in the scenario I, so their description and cost estimation (565000 €/pair) is the same as was described in the previous chapter.

A new heat exchanger is needed to cool the distillate from the stripper. Temperature of the distillate is around 42 °C and it must be cooled down to 30 °C. The stream is 17400 kg/h of benzene. The heat exchanger is a shell-tube type and cooling water used is 25 °C. By Aspen Plus simulation, the area of the exchanger was calculated to be 20 m^2 with 10000 kg/h of cooling water. Total cost estimation fort the heat exchanger with all the factors is 148000 €.

Some changes are required for the benzene distillation column's reboiler in scenario II. As was described earlier in chapter 9.2, the condensate of the reboiler must be redirected to lower pressure condensate tank in order to run the distillation column with a lower feed rate of 5000 kg/h. The total cost estimate for the condensate changes multiplied with all the factors is 62000 €.

Total investment costs for scenario II are 1676000 €.

11.1.3 Investments in scenario III

The only investment needed for scenario III is the redirection of the condensate flow from reboiler of the distillation column. In this scenario, no benzene is fed to the column during normal operation. However, the column must be in stand-by mode all the time. In order to make it feasible, the same changes as was described in previous chapter are needed. This means an investment cost of 62000 € for the scenario III.

11.2 Operating costs

The operating costs are calculated for clay, steam, and alkylation catalyst. The price difference of benzene with different quality is also taken into account. These costs are introduced next. All the operating costs for each scenario are also listed in Appendix 3.

11.2.1 Clay

In all the three scenarios, all benzene fed to the cumene unit is clay treated. The adsorption clay used for benzene purification is acid activated bentonite. According to laboratory tests, Clay A is the best in NFM removal, so it is recommended as adsorbent. The total cost estimate of clay changing is 8700 €. The estimation includes material costs, work costs, and costs regarding transportation and disposal. The estimation of work costs are based on history data. As there is not data available of disposal and transportation costs of clay, the estimation is based on history data of similar masses.

For the scenario I, where all the benzene is distilled over there should be no NFM in benzene. However, clay treating is still used due to possible disturbances in the process and lighter solvent decomposition products which might cause nitrogen residues in the benzene. The need for clay change is assumed to be once in every two years, when the total cost of clay is 8700 € every other year. According to laboratory tests, the saturation time for the clay was determined to be 8.7 months when NFM content of benzene is 2 ppm. This is the amount of NFM that is assumed to be in

self-produced benzene if it is not distilled over. This change period of 8.7 months is applied for the scenarios II and III, when the total cost of clay change per year is 12000 €.

11.2.2 Steam

Steam cost for all three scenarios is different. Steam pressure is 16 bar and it is assumed to cost 23 €/ton. The steam consumption and costs with different feed amounts of benzene are determined based on turn down ratio and the current operation of the column. The turn down ratio of the column is 40 % of maximum liquid loading of 21000 kg/h on higher trays. In the scenario I, all used benzene (22400 kg/h) is distilled over, so the steam consumption is the greatest, 5.6 ton/h, which makes annual cost of 1117000 €. In the scenario II, only the imported benzene (5000 kg/h) is distilled over, so the steam consumption is 2.4 ton/h. The annual steam cost is 467000 €. In the scenario III, no benzene is distilled over, but the distillation column must be in stand-by mode for any toluene peaks. The steam consumption for stand-by mode is 1.4 ton/h, which makes annual cost of 280000 €.

11.2.3 Catalyst

The costs regarding alkylation catalyst includes material costs as well as regeneration and transportation costs. For the catalyst, there are two possible alternatives for the costs. In the first alternative the catalyst is changed twice in a five year turnaround period, once in the turnaround and once between the turnarounds. In this case the total costs regarding two catalyst changes are 2516000 € per five year turnaround interval. The second alternative is to change the catalyst only once in a turnaround period, thus only in the turnaround. For the second alternative of one change the total costs are 1726000 € per five year turnaround interval. Thus, the cost difference is 790000 € per five years. With two changes, the catalyst would be changed on third and fifth year of the turnaround interval.

11.2.4 Benzene

The price of imported benzene differs depending on toluene content. Since imported benzene is anyway distilled, its toluene content can be higher in scenarios I and II than in scenario III where no benzene is distilled over. The higher the toluene content is, the cheaper the benzene is. 5 tons of imported benzene is used every hour. The difference in benzene price is not exactly known but a price difference of 10 €/ton of benzene is used for the calculations. With this price difference savings are 430000 € annually.

11.3 Financial indicators

Net present value (NPV), internal rate of return (IRR), and payback period (PBP) are calculated for all three scenarios. NPV tells the sum of present values of the future cash flows of a project. (Towler and Sinnott 2013) Here the NPV for all the scenarios are determined by benefit in annual cash flow achieved with processing changes. The benefit is determined for each year by subtracting operating costs of scenarios from operating costs of present situation and adding possible savings gained from benzene price. NPV is calculated according to equation (5). The discount rate used here is 10 % with time period of 10 years.

$$NPV = \sum_{t=1}^{T} \frac{B_t}{(1+r)^t} - C_0 \tag{5}$$

Where: B_t is benefit in cash flow in year *t* compared to present situation
C_0 is cost of initial investment
r is discount rate
T is number of years in the time period

Internal rate of return is the discount rate that makes the NPV of all cash flows of a project equal to zero. It tells the maximum interest rate that would still make the project break even during the time period. IRR is calculated according to equation (6). (Towler and Sinnott 2013)

$$\sum_{t=1}^{T} \frac{B_t}{(1+IRR)^t} - C_0 = 0 \quad (6)$$

Payback period is the time required to recover the cost of the investments of a project. As the benefits of years are uneven, PBP is calculated by determining the time that it takes for the cumulative benefits of years to match the investment costs (equation (7)). (Anon. H 2013) It is however assumed here that the benefits gained during one year are evenly divided through the year.

$$PBP = n + \frac{B_{c,n}}{B_{n+1}} \quad (7)$$

Where: n is the number of the last year when cumulative benefit is still lower than the investment costs

$B_{c,n}$ is the cumulative benefit at year *n*

B_{n+1} is the benefit at year *n+1*

The results are introduced in Table 9. Also investment costs, average operating costs per year, and benefit gained from different benzene quality are presented in the table. The detailed numbers and annual cost allocation of these calculations are presented in Appendix 4.

Table 9. CAPEX, OPEX, NPV, IRR, and PBP for the scenarios.

	Investment costs (€)	**Operating costs (€/a)** [1)]	**Benzene benefit (€/a)**	**NPV (€)**	**IRR (%)**	**PBP (a)**
Scenario I	1 260 000	1 467 000	430 000	1 157 000	30	2.6
Scenario II	1 676 000	824 000	430 000	4 688 000	61	2.0
Scenario III	62 000	795 000	0	3 747 000	996 [2)]	0.1 [2)]

[1)] Average operating costs per year in ten year time period

[2)] Small investment cost

As can be seen from the results, all the NPVs of all the scenarios are positive, thus feasible. However, for scenario II and III the NPV is remarkably higher than it is for scenario I. This is due to considerable large amount of steam consumed in scenario I. As the investment cost for scenario III is so small, the IRR is really high and the PBP

is so short compared to the other scenarios and these figures are not weighted as much on decision making. According to the NPV, the scenario II is the most profitable. Yearly development of the NPVs through the ten year period is shown in Figure 18. Different allocation of annual operating costs causes fluctuation in the NPVs.

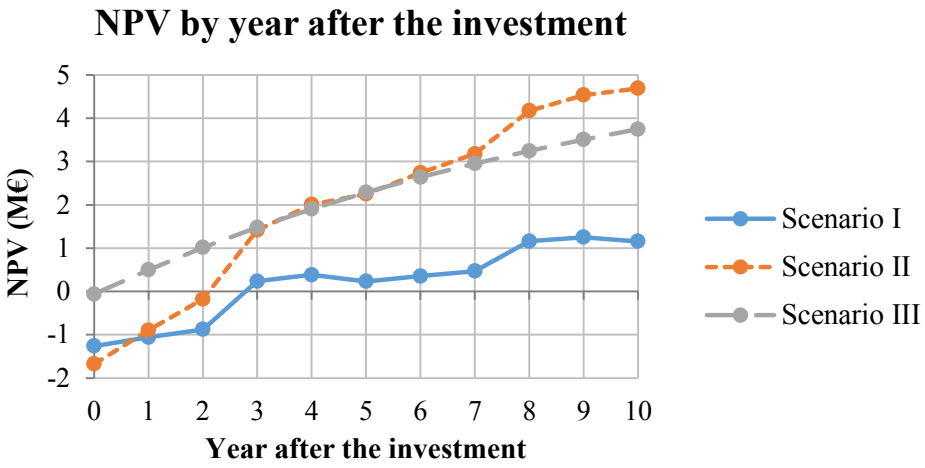


Figure 18. NPV by year after the investment.

11.4 Sensitivity analysis

Sensitivity analysis was conducted for net present value of the three scenarios. The discount rate and the time period are the same as previously, 10 % and 10 years. The variables in sensitivity calculations were the following: steam price, clay consumption, price difference of imported benzene, change in CAPEX and change in discount rate. Sensitivities of the NPVs of the scenarios are shown in Figures 19-23. The base case from the last chapter as well as 50 % and 150 % changes of each variable are marked as vertical grey line in all the figures. In the end of this chapter, in Table 10, the NPVs are shown when changing the variables from 50 % to 150 %. More accurate numbers of sensitivity analyses can be found in Appendix 5.

Steam price (Figure 19) is a variable that changes the NPV of scenario III the most. For the scenarios I and II the change in steam price is also important variable. When the steam price varies from 10 to 50 €/ton, the NPV of the scenario I changes from 1.88 M€ to -0.35 M€. For the scenario II the change of NPV is from 3.16 M€ to 7.87

M€ and for the scenario III from 1.57 M€ to 8.3 M€. For the scenarios II and III the steam consumption is lower than in present situation, so NPV rises with steam price. This is because the NPVs are calculated by cost benefit compared to the present situation. As the stem price gets over 42 €/t, the NPV of scenario III gets higher than of scenario II. It is however unlike that the steam price would get this high.

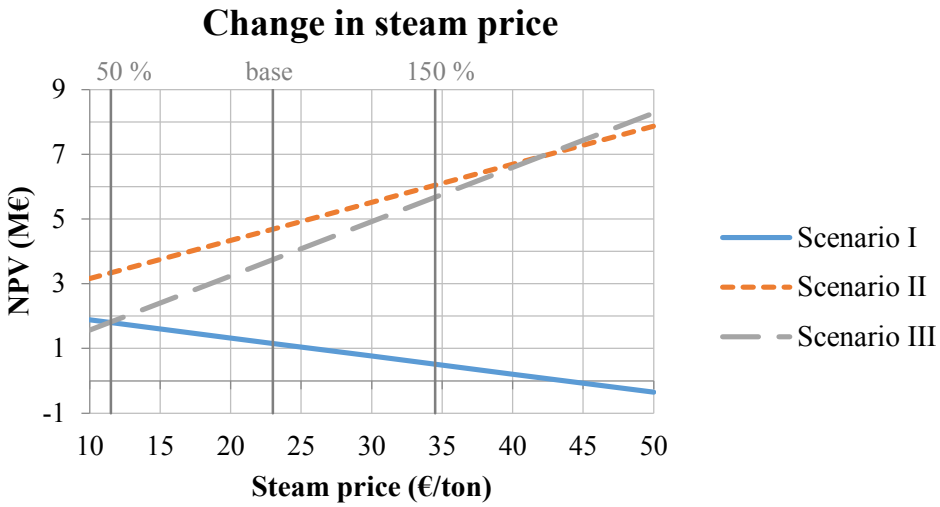


Figure 19. Steam price change effect on NPV.

As can be seen from the Figure 20, change in price difference of imported benzene is the variable that changes the NPV of both scenarios I and II remarkably. Scenario III is not taken into account in this case while there is no possibility to purchase lower quality benzene because the imported benzene is not distilled over in this scenario. For scenario I, the NPV varies from -1.49 M€ to 3.80 M€ as the benzene price difference compared to higher quality benzene changes from 0 to 20 €/ton of imported benzene. The NPV of scenario I drops to negative side as soon as the price difference is under 5.6 €/ton. As for the scenario II, the change in NPV varies from 2.05 M€ to 7.33 M€.

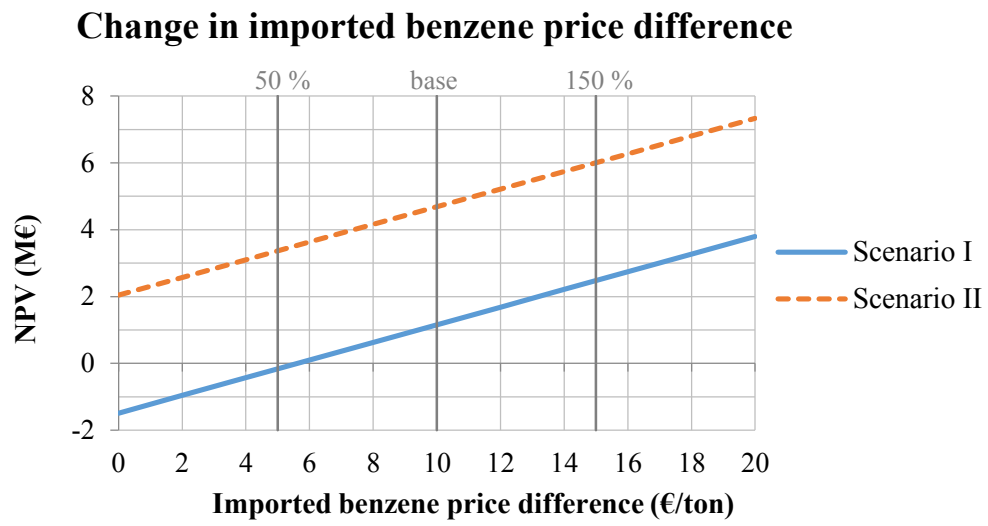


Figure 20. Imported benzene price change effect of NPV.

The effect of clay consumption on NPV is calculated by changing NFM concentration of benzene, which affects the saturation time of the clay. The scenario I is not included in this figure while all the benzene is distilled over, so it should not contain any NFM. It can be stated that clay consumption change does not affect the NPVs of scenarios II and III much (Figure 21). In both the scenarios the NPV change is in 0.22 M€ although the saturation time is almost seven times shorter as the NFM concentration is raised from 1 to 7 ppm.

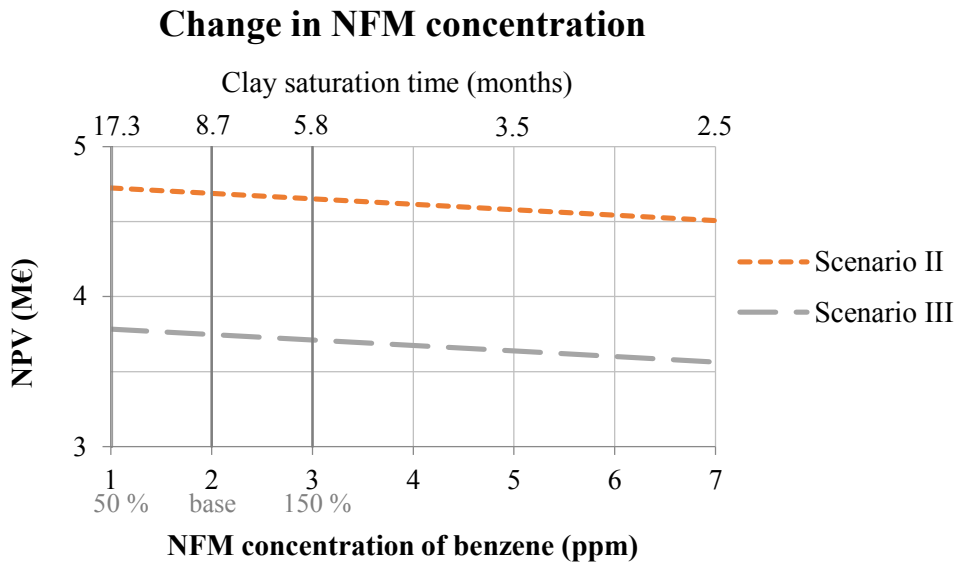


Figure 21. NPV affected by clay consumption change due to NFM concentration change in benzene. Saturation time of clay in months is presented above the charts.

Changing investment costs from 50 % to 150 % (Figure 22) of the original value has some effect on the NPV of scenarios I and II. However, the investment costs for scenario III are so small that the change hardly effects the NPV, only 62 000 € at most. For the scenario I, the NPV varies from 1.79 M€ to 0.53 M€, and for the scenario II from 5.53 M€ to 3.85 M€.

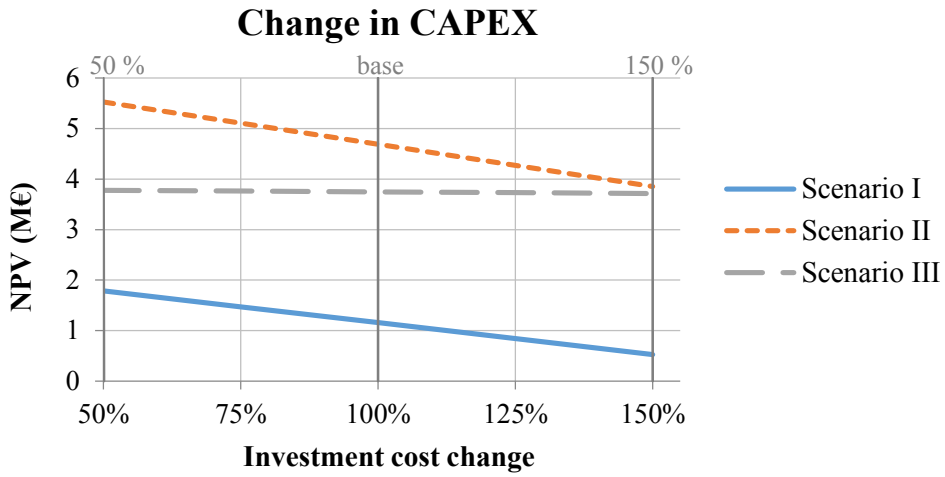


Figure 22. Investment cost change effect on NPV.

Variation of discount rate changes the NPV of the scenarios as is shown in Figure 23. The higher the discount rate is, the lower the NPV is for all the scenarios. Effect of discount rate change on NPV is highest for the scenario II. As the discount rate gets over 23.5 %, the NPV of the scenario III gets higher than of the scenario II.

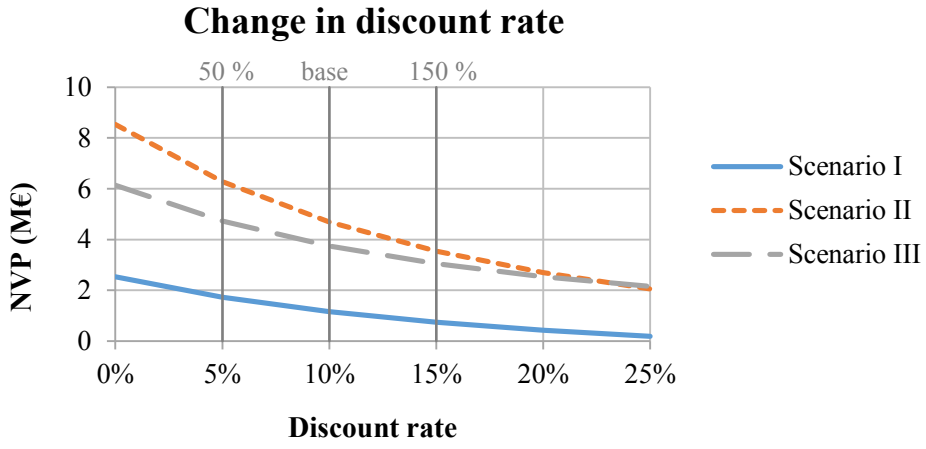


Figure 23. Discount rate change effect on NPV.

Table 10. The NPVs when changing the variables from 50 % to 150 %.

		NPV (M€)				
		Steam price	**Imported benzene price**	**Clay consumption**	**Investment costs**	**Discount rate**
Scenario I	50 %	1.80	-0.16		1.79	1.73
	100 % (base)	1.16	1.16		1.16	1.16
	150 %	0.51	2.48		0.53	0.74
Scenario II	50 %	3.33	3.37	4.72	5.53	6.27
	100 % (base)	4.69	4.69	4.69	4.69	4.69
	150 %	6.04	6.01	4.65	3.85	3.55
Scenario III	50 %	1.82		3.78	3.78	4.73
	100 % (base)	3.75		3.75	3.75	3.75
	150 %	5.68		3.71	3.72	3.05

As can be seen from Table 10, scenario I is most sensitive for change in benzene price difference, whereas scenarios II and III are both most sensitive for price difference of steam.

12 Discussion and recommendations

According to the net present value, the scenario II is financially most feasible. There is however other factors that must be considered before the final decision on which one of the scenarios is recommended.

In the scenario I, a negative factor is the distillation of all self-produced benzene. This consumes a large amount of steam and is most of the time unnecessary. However, the distillation of all used benzene gives maximum protection of the alkylation catalyst as the risk of sudden NFM peaks or other heavy impurities in the feed to the cumene unit is very low. This enables the catalyst to run through the whole five year turnaround period. Another great plus of this scenario is the possibility to purchase benzene with higher toluene content. The availability and price of this quality benzene is much better than for the currently desired quality.

As for the scenario II, there are many positive factors. Only the imported benzene is distilled over, so there is no unnecessary distillation of self-produced benzene and steam consumption is low. There is however possibility for toluene or NFM peaks in the benzene but as the distillation column is in use for imported benzene, the self-produced benzene can easily be redirected to the distillation column and this way deactivation of the catalyst can be avoided. In this scenario there is also the possibility to purchase lower quality benzene, which is a great advantage in the long term.

In the scenario III, the most important consideration is that there is no possibility for the lower quality imported benzene, while it is not distilled over. It can be assumed that the availability of benzene with the currently desired purity will be uncertain in the future. At worst, it could lead to a situation where the capacity of the cumene unit cannot be met, as the desired benzene is not available. In this scenario, there is also a relatively high risk of toluene or NFM peaks in benzene. As the distillation column is not in use but only in a stand-by mode, it would take a while to be able to redirect the benzene to the distillation column. For this scenario, there is a need for two catalyst changes in one turnaround period. The positive factor in this scenario is that the steam consumption is as low as possible.

The most important factors of the decision making are summarized in Table 11.

Table 11. The most important pros (+) and cons (-) of the scenarios.

	Scenario I	**Scenario II**	**Scenario III**
Imported benzene with higher toluene content	+	+	-
Avoid to distil on-spec benzene	-	+	++
Catalyst run length match the turnaround period	++	+	-
NPV	-	++	+

According to all the considered factors, the scenario II is recommended to be the processing method for benzene. It has the most pros and no cons. Its financial

indicators are also very good. By choosing the scenario II, remarkable annual savings in OPEX could be achieved, mostly in steam and catalyst costs. Also savings from different quality benzene are remarkable. Regarding the clays, the currently used clay A is recommended to be used also in the future as it has the best adsorption capability and capacity for NFM.

Clay tower operation needs some further consideration. If the towers are operated only one at the time, it would need an online analysis for NFM. As the analysis would indicate NFM, the process feed should be immediately directed to the other tower and the clay changed in the other. Another option is that the towers would be filled and operated with so called lead-lag method. This means that the process stream is fed through both of the towers filled with clay and samples are taken between and after the towers. As a sample between the towers indicates NFM in the stream, the feed would be directed through only the second tower and the clay in the first tower would be changed. As soon as the clay is changed, the feed would be directed through both of the towers. This way the risk of NFM in the product could be minimized. Regarding the clay treating, the pressure drop in the clay towers is considerable. This would be a problem at least in the scenario III where new pumps are not used. However, clay B and especially clay C, are supposed to have lower pressure drop than clay A. This is a factor that should be considered if the pressure drop is too high with clay A. Another option is to not to use the maximum amount of clay in the towers, but to fill them only partly to reduce the pressure drop.

13 Conclusions

In this work, a techno-economic comparison of three possible benzene processing scenarios in Borealis' aromatics production unit was made. The scenarios were: I) distillation of all used benzene, II) distillation of only imported benzene, and III) bypassing the benzene distillation column completely. The most important targets of processing changes were: to be able to purchase benzene with higher toluene content, to avoid distillation of benzene that is on specifications, and to allow the alkylation

catalyst run length match the turnaround interval of five years. In order to study the possibility to implement the scenarios, some simulations of the distillation column, laboratory tests of clay purification, and financial calculations were conducted.

According to the simulations, the capacity of the benzene distillation column for maximum feed in the scenario I is enough. The maximum capacity was determined by flooding factors of the trays with different feed amounts and reflux ratios. As for the minimum capacity of the column for the scenario II, reboiler of the column is the limiting factor. If the steam feed to the reboiler is too low, it causes said hammering. However, the amount of steam required to avoid the hammering is so high that it would not be feasible to distill only the imported benzene. So, redirection of condensate to a tank with lower pressure is required to reduce the steam amount. After redirection of the condensate, minimum feed of the scenario II as well as stand-by mode for the scenario III would be possible.

Three different clays (A, B, and C) were tested in laboratory for NFM removal. NFM is used as a solvent in extractive distillation of self-produced benzene. Thus, NFM removal is important for scenarios II and III where the self-produced benzene is not distilled over. Both adsorption capabilities and capacities of the clays were tested. It turned out that clay A outperformed the other clays both in adsorption capability and capacity. Thus, clay A is recommended for removal of NFM. According to the capacity tests, the saturation times for clay beds in the process were calculated.

The financial viability of the scenarios was estimated by NPV, IRR, and PBP. First, estimations of all investment needs and costs as well as operating costs for each scenario were conducted. The NPVs were calculated based on benefit gained in operating costs with process changes compared to the present situation. The most remarkable savings are gained in steam consumption and lower price of benzene when purchasing it with higher toluene content. NPV for the scenario II proved to be the best. Sensitivity analysis was conducted with variables of steam price, clay consumption, price difference of imported benzene, change in CAPEX, and the

change in the discount rate. The price of steam and imported benzene are the most significant operating cost variables for the sensitivity of NPVs.

In addition to the best NPV, also other factors imply on behalf of selecting the scenario II. Although in the scenario I the catalyst protection is the best, it has the largest steam consumption of all the scenarios. Most of the time the self-produced benzene is however on specifications and distillation is not required. As for the scenario III, the risk of the catalyst deactivation due to heavy impurities is the highest as no benzene is distilled over. The scenario III is also the only one with no possibility to purchase benzene with higher toluene content. In the future, this can be a considerable problem as the availability of high quality benzene is not certain. This could lead to a situation where the benzene demand of the cumene unit cannot be met. In the scenario II, all the initial targets are achieved. There is the possibility to purchase lower quality benzene, no benzene that is on specifications is distilled over, and the catalyst run length should match the turnaround period with efficient operation of the clay treaters. According to these factors and the financial calculations, the scenario II is recommended to be the processing method for benzene.

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Appendix 1

Results of the clay tests

Adsorption capability tests for NFM removal						
	T, °C	**NFM concentration, ppm**				
Time from start		start	~22 min	~50 min	~77 min	~108 min
Clay A						
Test 1/1	30	105.5	0.9	1.3	3.9	8.8
Test 2/1	23 (room)	89	2.3	1.7	7.7	15.3
Test 3/1	40	86	2.1	1.1	1.4	5
Test 1/1, repetition	30	92	0	1.1	4.6	7.14
Clay B						
Test 1/2	30	78	19.8	26.5	32.8	38.5
Test 2/2	23 (room)	94	27.7	41	47	49.1
Test 3/2	40	84	10.9	23.3	28.8	38.6
Clay C						
Test 1/3	30	73	28.8	41.5	44.9	48.6
Test 2/3	23 (room)	74	37.4	43.5	48.3	53.3
Test 3/3	40	73	22	28.8	37.9	39.2

Capacity tests for NFM						
	Solution, g	**NFM concentration, ppm**		**NFM in solution, g**		
Test time 20 h		start	end	start	end	removed
Clay A	426.5	353.4	93.4	0.1507	0.0398	0.1109
Clay B	426.15	352.9	184.3	0.1504	0.0785	0.0718
Clay C	425.96	349.1	226.9	0.1487	0.0967	0.0521

Adsorption tests for other components				
	Time, min from start	**Methanol, ppm**	**Phenol, ppm**	**NMP, ppm**
Clay A	start	60	90	67
	10		46.6	
	28	60	71.1	0
	45.5	60	62.7	
	64.5		81	0
	83.5		83.5	
	100.5	60	90.4	0.4
Clay B	start	57	170	105
	8.5	57	103.5	
	26		130.2	0
	44.5		142.7	
	64.5		153.2	4.1
	83.5		168.3	
	101		178.7	9.1

Instructions for clay tests in laboratory

1. Materials

Clays

- Clay A
- Clay B
- Clay C

Chemicals

- Benzene 99.9 %

Test substances

- N-formylmorpholine (NFM)
- 1-methyl-2-pyrrolidone (NMP)
- Phenol
- Methanol

2. Equipment

Equipment used for clay tests is a 70 ml glass column with a water circulation for temperature adjustment, a sinter and a valve to adjust the flow.

Analyses are done with gas chromatography (GC).

Other equipment:

- Scale
- Water bath
- Timer

3. Methods

Adsorption capability test in general

Adsorption test is conducted to have information about changes in clay efficiency during a two hour test. 5 g of clay is placed into the test equipment through which the test solution is drained by gravity. The flow velocity is adjusted by the valve and the temperature is adjusted by the water circulation. Clay performance is tested in different temperatures (20, 30 and 40 °C). A sample is taken of the test solution before the clay treatment. Solution is drained for 15 minutes to 100 ml bottle after which the bottle is switched to a new one. A sample is taken from every other bottle and analyzed with GC. Test arrangement is presented in Figure 1/A2.

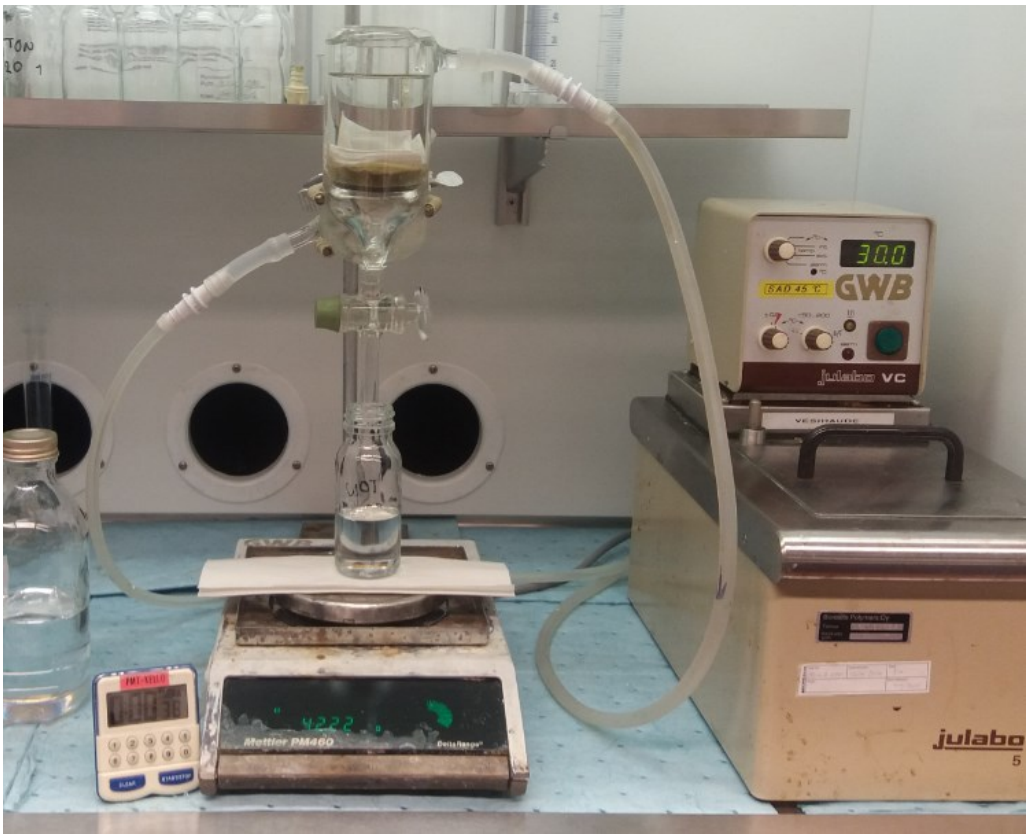

Figure 1/A2. Test arrangement for adsorption capability test.

Performing the adsorption capability test

1. Put the water bath and the water circulation on.
2. Make the test solution according to the recipe. Analyze the solution with GC.
3. Weight the clay (5 g) and place it into the test equipment.
4. Poor test solution to the equipment so that the liquid surface is about 7 cm above the clay bed.
5. Adjust the flow velocity using a timer and a scale. Leave the valve in correct position.
6. Pour the test solution into the equipment through the test so that the level of the liquid remains as stable as possible.
7. Monitor the flow velocity during the test and adjust the valve position if needed.
8. Drain the solution for 15 minutes to 100 ml bottle and switch to a new one. During the test eight bottles are collected.
9. Take samples from second, fourth, sixth and eight bottles and analyze the samples with GC.
10. Wash the used equipment.

Test conditions for adsorption tests

All following three tests are conducted for all three clays:

Adsorption capability tests			
	Time	2	h
Test 1	T	**30**	°C
	Flow	360	g/h
	NFM	100	ppm
Test 2	T	**20**	°C
	Flow	360	g/h
	NFM	100	ppm
Test 3	T	**40**	°C
	Flow	360	g/h
	NFM	100	ppm

Capacity tests for NFM adsorption in general

In capacity tests the adsorption capacity of the clay to remove NFM is tested during a 20 hours test. Test is conducted by adding 1 g of clay to about 425 g benzene solution. NFM concentration of the solution is analyzed before the test. The exact mass of the solution is also weighted before the test. The bottle is placed horizontally in a shaker to maximize the mixing of the clay and the solution. The test is conducted in room temperature (23 °C). After 20 hours of shaking the bottle is placed vertically on table and the clay is let set on the bottom. Then about 50 ml sample is taken and analyzed with GC.

Adsorption test for other components

Clay's ability to remove NMP, phenol and methanol are tested. The test is conducted with same method as NFM tests but the flow velocity is 90 g/h and clay amount is 10 g. Test temperature is 30 °C.

CAPEX and OPEX of the scenarios

Investments		
Scenario I: Distillation of all used benzene		
Pumps	565000	€
Pipes, 1080 m	695000	€
Total	**1260000**	**€**
Scenario II: Distillation of imported benzene		
Pumps	565000	€
Pipes, 1400 m	901000	€
Heat exchanger	148000	€
Condensate redirecting	62000	€
Total	**1676000**	**€**
Scenario III: Bypassing the benzene distillation column		
Condensate redirecting	62000	€
Total	**62000**	**€**

Operating costs		
	Scenario I	**Scenario II**
Clay	8700 €/change every 24 months	8700 €/change every 8.7 months 12000 €/a
Catalyst	1726000 €/change 1 change/TA period	1726000 €/change 1 change/TA period
Steam, 23 €/t	48600 t/a 1117000 €/a	20300 t/a 467000 €/a
Benzene savings, price diff. 10 €	+430000 €/a	+430000 €/a
	Scenario III	**Present situation**
Clay	8700 €/change every 8.7 months 12000 €/a	8700 €/change every 24 months
Catalyst	1258000 €/change 2 changes/TA period	1258000 €/change 2 changes/TA period
Steam, 23 €/t	12200 t/a 280000 €/a	39500 t/a 908000 €/a
Benzene savings, price diff. 10 €	0 €/a	0 €/a

Financial indicators of the scenarios

	Year	0	1	2	3	4	5	6	7	8	9	10
Present situation	Utilities		Steam	Steam, Clay	Steam, Catalyst	Steam, Clay	Steam, Catalyst	Steam, Clay	Steam	Steam, Clay, Catalyst	Steam	Steam, Clay, Catalyst
	Oper. costs, €		908000	917000	2166000	917000	2166000	917000	908000	2174000	908000	2174000
Scenario I	Utilities		Steam	Steam, Clay	Steam	Steam, Clay	Steam, Catalyst	Steam, Clay	Steam	Steam, Clay	Steam	Steam, Clay, Catalyst
	Oper. costs, €		1117000	1126000	1117000	1126000	2843000	1126000	1117000	1126000	1117000	2852000
	Benzene savings, €		430000	430000	430000	430000	430000	430000	430000	430000	430000	430000
	Benefit, €		221000	221000	1478000	221000	-247000	221000	221000	1478000	221000	-247000
	Present value, €	1260000	44000	40000	982000	33000	-260000	27000	25000	609000	21000	-162000
	NPV	1157000	€	IRR	29.7	%	PBP	2.55	years			

	Year	0	1	2	3	4	5	6	7	8	9	10
Scenario II	Utilities		Steam, Clay	Steam, Clay	Steam, Clay	Steam, Clay	Steam, Clay, Catalyst	Steam, Clay	Steam, Clay	Steam, Clay	Steam, Clay	Steam, Clay, Catalyst
	Oper. costs, €		479000	479000	479000	479000	2205000	479000	479000	479000	479000	2205000
	Benzene savings, €		430000	430000	430000	430000	430000	430000	430000	430000	430000	430000
	Benefit		859000	868000	2117000	868000	391000	868000	859000	2125000	859000	400000
	Present value, €	1676000	624000	575000	1461000	475000	136000	393000	352000	911000	291000	88000
	NPV	4688000	€	IRR	61.3	%	PBP	1.98	years			
Scenario III	Utilities		Steam, Clay	Steam, Clay	Steam, Clay, Catalyst	Steam, Clay	Steam, Clay, Catalyst	Steam, Clay	Steam, Clay	Steam, Clay, Catalyst	Steam, Clay	Steam, Clay, Catalyst
	Oper. costs, €		292000	292000	1550000	292000	1550000	292000	292000	1550000	292000	1550000
	Benzene savings, €		0	0	0	0	0	0	0	0	0	0
	Benefit, €		616000	624000	616000	624000	616000	624000	616000	624000	616000	624000
	Present value, €	62000	560000	516000	463000	426000	382000	352000	316000	291000	261000	241000
	NPV	3747000	€	IRR	996.5	%[1)]	PBP	0.1	years[1)]			

[1)] Small investment cost

Sensitivity analysis

Steam price				
€/t	NPV (€)			
Steam price	Scenario I	Scenario II	Scenario III	
10	1884000	3157000	1567000	
20	1324000	4335000	3244000	
23	**1157000**	**4688000**	**3747000**	base case
30	765000	5513000	4921000	
40	206000	6691000	6598000	
50	-353000	7868000	8274000	

Imported benzene price			
€/t	NPV (€)		
Benzene price difference	Scenario I	Scenario II	
0	-1486000	2046000	
2	-957000	2574000	
4	-429000	3103000	
6	100000	3631000	
8	628000	4160000	
10	**1157000**	**4688000**	base case
12	1685000	5217000	
14	2213000	5745000	
16	2742000	6274000	
18	3270000	6802000	
20	3799000	7330000	

Change in clay consumption					
	NPV (€)		Saturation time	Changes/year	
NFM, ppm	Scenario II	Scenario III	months		
1	4725000	3783000	17.3	0.7	
2	**4688000**	**3747000**	**8.7**	**1.4**	base case
5	4579000	3637000	3.5	3.4	
7	4505000	3564000	2.5	4.8	

Change in investment costs				
	NPV (€)			
Investment	Scenario I	Scenario II	Scenario III	
50 %	1787000	5526000	3778000	
75 %	1472000	5107000	3762000	
100 %	**1157000**	**4688000**	**3747000**	base case
125 %	842000	4269000	3731000	
150 %	526000	3850000	3716000	
Change in discount rate				
	NPV (€)			
Discount rate	Scenario I	Scenario II	Scenario III	
0 %	2526000	8537000	6139000	
5 %	1728000	6273000	4725000	
10 %	**1157000**	**4688000**	**3747000**	base case
15 %	737000	3545000	3049000	
20 %	422000	2699000	2536000	
25 %	179000	2056000	2150000	